KINETIC STUDIES OF COKE FORMATION IN HYDROCARBON FRACTIONS OF DIFFERENT BITUMENS UNDER VARIOUS CONDITIONS

FINAL REPORT

by

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KINETIC STUDIES OF COKE FORMATION IN HYDROCARBON FRACTIONS OF DIFFERENT BITUMENS UNDER VARIOUS CONDITIONS

INTRODUCTION

Because of increasing commercial demands for the lighter hydrocarbons, there is currently much interest in converting heavier hydrocarbons into lighter fractions. Hydrocracking processes are commonly used for liquefying coal, or heavy residual or distillate oils, with the formation of lower-boiling products.

In Canada synthetic crude oil is produced from bitumen by hydrotreating it, a process that also removes hetero atoms. This is an alternative process for producing synthetic oil. Hydrotreating is perhaps the single most significant advance in petroleum refining technology over the last few decades.

Hydrogenation, a process generally used to improve product quality, may be destructive or non-destructive. Hydrocracking is a destructive process, characterized by the cleavage of carbon-carbon bonds accompanied by addition of hydrogen. In non-destructive hydrogenation, product quality is improved by the removal of nitrogen, sulfur and oxygen, with the formation of ammonia, hydrogen sulfide and water, respectively.

Many previous investigations have thrown light on the characteristics of hydrogenation processes. Speight [1] reported that during hydrocracking processes there are considerable changes in the organic structures, and that there is a loss of nitrogen, sulfur and oxygen. He also concluded that coke formation occurs as a result of polycondensation of aromatic nuclei. Figure 1 shows a typical reaction mechanism for the hydrocracking of the model compound naphthalene. Figure 2 shows the types of processes involved in the removal of a hetero atom, nitrogen. During hydrocracking several types of products can be

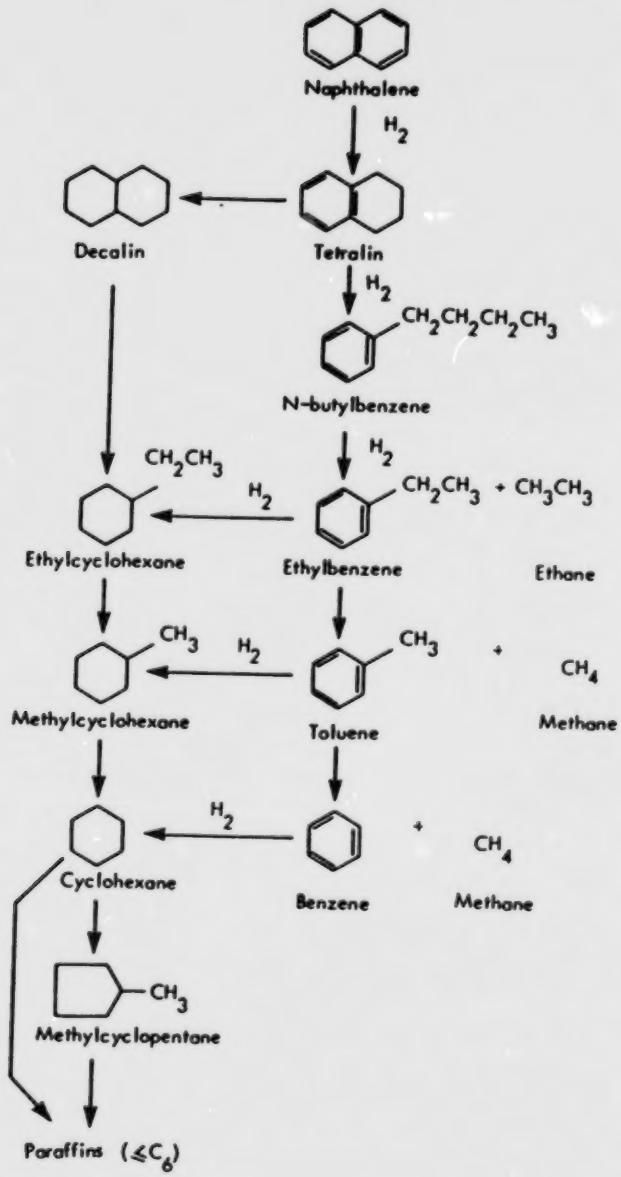

Figure 1: A reaction scheme for the hydrocracking of naphthalene (ref. 1).

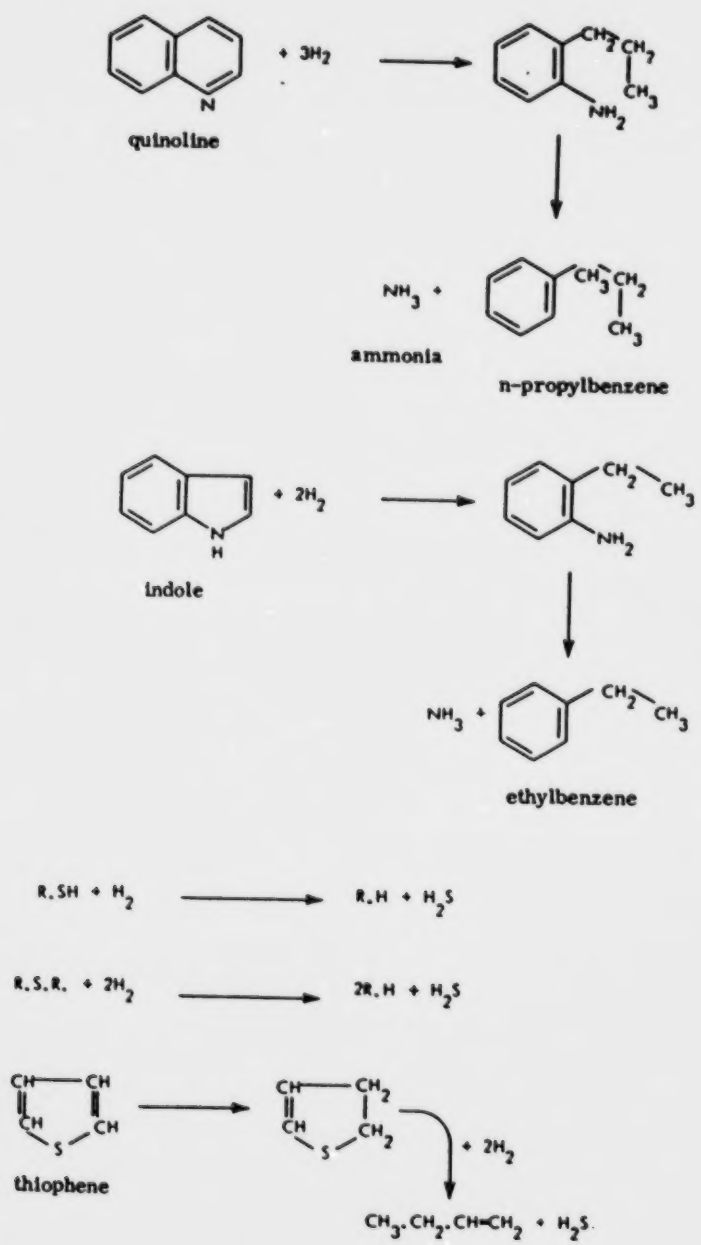

Figure 2: Reaction schemes for the hydrocracking of compounds containing heteroatoms (N and S), showing how these atoms are removed in the process (ref. 1).

formed, depending on the reaction conditions. In the scheme shown in Figure 1 for naphthalene, one aromatic ring is activated and cracked, with the formation of n-butyl benzene. Also, both rings may become saturated and cracked, with the formation of ethyl cyclohexane. These products further break down into volatile substances.

During the hydrocracking of petroleum a certain amount of polymer material, such as tar and coke, is always formed along with the light products. Coke, a solid product of the process, is formed by polymerization of unsaturated substances. The formation of coke during the thermal and catalytic hydrocracking of bitumen and heavy oils presents as major difficulty, since the operating life of a reactor is severely limited by the formation of a carbonaceous deposit on the catalyst and on the walls of the reactor. This causes expensive shutdowns of the process, and possibly requires a complete renewal of the catalyst system.

Shiboaka et al [2] concluded from their investigations that hydrogenation and coke formation occur simultaneously, the relative importance of the two processes depending on the hydrogen pressure. When this is high the hydrogenation predominates, while when the hydrogen pressure is lower the coking becomes more important.

Koji Ouchi et al. [3] have studied the formation of coke during the hydrocracking of asphaltene prepared from Japanese coal. They found that in the hydrogenation of asphaltene or tar-pitch, coking still takes place even at a temperature as high as 450^{o}C and at a hydrogen pressure as high as 12 MPa. Geoffrey et al. [4] found that during the hydrogenation of British coals, the tar produced was of higher aromaticity than that formed when pyrolysis is carried out in an atmosphere of nitrogen. The aromaticity of the tars was

increased by increasing the hydrogen pressure, but was hardly affected by increasing the nitrogen pressure.

Up to now little work has been done on the hydropyrolysis of asphaltenes from coal [5,6], and hardly any kinetic studies have been made. Recently Phillips and coworkers [7] have reviewed the kinetics of the thermal cracking of bitumen. Wilson et al [8] described work on the up-grading of oil-sand bitumen. The present authors [9,10,11] have made systematic and detailed studies of the kinetics of coke formation during the pyrolysis of bitumen and its fractions, in an atmosphere of nitrogen.

During recent years various workers [12-16] have demonstrated the beneficial influence of sulfur and sulfur compounds, particularly hydrogen sulfide, on the liquefaction of coals; some decrease in coke formation has been brought about. No kinetic studies of the influence of sulfur or sulfur compounds have, however, been reported.

Objects of the Present Work

In view of the state of knowledge of cracking and hydrogenation processes, particularly in connection with coke formation, some kinetic studies have been carried out, and are described in the present report. The work has had three main objects, as follows:

(1) A preliminary object was to separate bitumens into various fractions, and to characterize these fractions. Bitumen is a highly complex mixture of many compounds, and an understanding of the cracking of bitumen will be aided by studies on the individual fractions.

(2) The second object was to gain knowledge of the kinetics of coke formation from various fractions, during pyrolysis in an inert atmosphere of nitrogen, with the addition of various amounts of sulfur.

(3) The third object was to understand the kinetics of the hydrocracking of the bitumen fractions. This work involved the design and assembly of special high-pressure equipment, and led to conclusions as to the mechanisms of the processes.

The kinetic studies were carried out with the following two bitumens, supplied by the Energy Research Laboratory of CANMET:

(1) Cold Lake Bitumen, 21-CL-81

(2) Light Arabian vacuum bitumen (pitch), 25-ARA-81.

Analyses of these heavy crudes were supplied to us by CANMET and are reproduced in Table 1.

Table 1

Analyses of Bitumens

	Cold Lake	Arabian
Gravity, API	4.95	6.82
Specific gravity 60/60°F	1.031	1.023
Sulfur, wt %	5.90	4.54
Carbon, wt %	83.13	84.91
Hydrogen, wt %	10.02	9.81
Nitrogen, wt %	0.42	0.21
Ash, wt %	0.01	0.03
Vanadium, ppm	231	144
Nickel, ppm	82	30
Iron, ppm	41	38
Pentane insoluble, wt %	27.0	17.8
Toluene insoluble, wt %	0.02	0.04

PART I - SEPARATION OF BITUMENS INTO DIFFERENT FRACTIONS

EXPERIMENTAL

During recent years there have been major improvements in the analysis of crude oil [17]. The separation and analysis of high-boiling fragments are complicated and time-consuming procedures. Techniques for the fractionation of petroleum have been described in detail by Speight [1] and Rossini [18]. In addition, several American Petroleum Institute standard methods are available, including:

1) dimethylsulfoxide extraction (IP 346/80)*
2) silica gel adsorption (ASTM-D-1319-70)
3) sulfonation (ASTM-D-1019-68)

The procedures employed in the present work, used for all of the bitumens studied, were selected from the above, to suit our particular requirements, and are as follows:

According to ASTM-D2006, deasphaltenation of bitumen is carried out by precipitation with 40 times its volume of n-pentane; n-heptane is also recommended for this purpose. The following method [19] was found to give highly reproducible results:

5 g of bitumen was dissolved in 5 mL of benzene in a conical flask. To this was added 200 mL of n-pentane (HPLC grade, from Fisher Scientific), with thorough shaking. The flask was kept in the dark for 10 hours with occasional shaking. The contents were then filtered through a sintered crucible, and the precipitate washed with n-pentane as long as a clear solution was obtained. The n-pentane extract was kept for later treatment. The precipitate in the

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* API procedures are listed on p. .

crucible was dissolved in a minimum amount of benzene which was then distilled under vacuum. The material was then kept for half an hour at 100°C, after which it was completely dry. Since asphaltene is sensitive to atmospheric oxygen, care was taken not to expose it to the atmosphere for too long. The dark brown precipitate, consisting of asphaltene, was weighed and its yield calculated; it was then stored in a vacuum desiccator. Since this procedure is very sensitive to factors such as the quantity of n-pentane used, the temperature, and the time taken to perform the operations, care was taken to reproduce the conditions in subsequent separations. Experiments were repeated about ten times, with reproducibility of ± 1.5%. The results are shown in Table 2.

Further separation of the n-pentane extract was carried out by the technique of adsorption column chromatography. Maltene was first separated into resins and oil by the Syncrude analytical method (also recommended in ASTM-D-2007-80), a benzene-acetone 50/50 mixture being used as eluent. Attapulgus clay was used as the adsorbing material. The commercial attapulgus clay, grade AX-1799, was supplied by Matheson, Coleman and Bell Manufacturing Chemists, Norwood, Ohio. This clay, in the form of a fine powder, was pressed hydraulically and the cake formed was crushed, the resulting fine particles being sieved to 30-60 mesh. It was then activated at 300°F for 3 hours, transferred hot into a closed bottle and kept in a desiccator for further use.

A 65 mL volume of the activated clay was packed into the chromatographic column of the recycling system. The apparatus consisted of a 500 mL kettle having two necks. The chromatographic column (22 x 450 mm in size), with an insulated jacket, was mounted on one neck; a distillation tube was on the other neck. A condenser was attached at the top of the column, which is also connected to the

Table 2

Relative percentage of the components of bitumen (wt%)

	Cold Lake	Arabian
Asphaltene	24.47	15.95
Soft resin	23.98	24.98
Hard resin	2.99	3.63
Aromatics	31.94	32.13
Saturates	15.96	22.35

A total of 50 experiments were done on the separation of the five fractions from two bitumens.

distillation tube by means of a side arm. The kettle was heated by a mantle having a temperature-controlled system. Thermostatted hot water at the required temperature was circulated through the jacket of the distillation tube, in order to allow the vapour from the kettle to reach the condenser. The condensed liquid dropped into the chromatographic column and finally entered the kettle, the required compound being eluted. Recycling thus is accomplished. After the elution of one component another solvent was placed in the kettle, in order to extract another component; the process was continued in this way.

The n-pentane extract, after removal of asphaltene, was concentrated to about 20 mL by evaporating the solvent in a rotary evaporator. The clay in the column was treated with 50 mL of n-pentane, and the concentrated maltene solution added to it. The kettle was charged with 200 mL of n-pentane and refluxing continued for 2 hours; the n-pentane elutes the oil and returns to the kettle. When all of the oil was eluted, the system was cooled, the kettle replaced, and the column dried by purging with nitrogen. The column now retained the resins.

The kettle was next replaced by another kettle containing 200 mL of methyl ethyl ketone (MEK) of high purity (obtained from Fisher Scientific), and the system was refluxed for 2 hours. Methyl ethyl ketone extracts soft resin from the clay, and hard resin is retained in the column. After the soft resin elution was completed, the column was dried by nitrogen as before.

The kettle was again replaced with another kettle containing 200 mL of tetrahydrofuran (histological grade, obtained from Fisher Scientific) and 10 mL distilled water (added to prevent explosion due to peroxide formation). Tetrahydrofuran (THF) extracts hard resin from the column and returns to the kettle,

the whole operation taking about 2 hours. A change in colour of the THF solution indicated when the extraction was complete.

The MEK and THF extracts were evaporated in a rotary evaporator under vacuum to the minimum possible amount. They were then transferred to evaporating dishes, and the rest of the solvent evaporated, over a long period, in a vacuum desiccator. The resins were finally dried completely in an oven at 100°C for 10 minutes, and then kept in a closed bottle which was placed in a vacuum desiccator. The yield was determined.

The soft resin was obtained as a dark coloured highly dense oily liquid. The hard resin was a dark coloured crystalline semi-solid. Their percentages are given in Table 2.

The pentane extract obtained from the clay, containing oil, was further fractionated into aromatics and saturated hydrocarbons. The aromatic portion usually contains polycondensed aromatic rings with aliphatic side chains. The saturated fraction is mainly naphthenic in nature with some long-chain paraffins.

The separation of oil was carried out by the ASTM-D1319-70 method, with modifications according to ASTM-D2549-81. A chromatographic column (900 x 10 mm) was filled with 60 mL of activated silica gel (100 - 200 mesh, grade 923) obtained from Davison Chemicals, Baltimore, Maryland. Above the silica gel was another 5 mL of activated alumina of grade AX-0612-3, type F-20, 80-200 mesh, obtained from MCB Manufacturing Chemists, Cincinnatti, Ohio. Silica gel and alumina were both activated each time prior to use, by heating to 300°F for 3 hours. The column was first filled with n-pentane, to which silica gel was added slowly with continuous vibration of the column; care was taken to avoid any air gap inside the packed column. Alumina was then added by following a

similar procedure. Uniform packing throughout the column length was then achieved by gentle admission of nitrogen at a slightly increased pressure. Care was taken to prevent the pentane level from falling below the alumina.

The oil containing the pentane extract was concentrated to about 5 mL in a rotary evaporator. This liquid was then injected into the alumina by means of a syringe. The column was then eluted with 200 mL of n-pentane by applying a gentle nitrogen pressure through the column; this helps to avoid any channelling of the column and also gives a uniform flow of liquid. The pentane carried the saturated portion with it, the aromatic portion being retained inside the packing material. Since saturates are colourless, the pentane solution was clear. The completion of the elution was tested by ultraviolet spectrophotometry.

Since aromatics are coloured, it was easy to observe that they are retained in the column, and that they do not contaminate the saturates. The aromatics were eluted from the column with approximately 80 mL of toluene; the complete elution of the aromatics was easily observed visually.

The pentane and toluene were both evaporated from the compounds in a rotary evaporator. The residues were dried in an oven at $100^{o}C$ for half an hour. The dried material was weighed and its yield calculated; the percentages are given in Table 2.

Other methods besides the ASTM methods were also tried. One technique used was High Performance Liquid Chromatography (HPLC), which is rapid but not highly efficient for large quantities such as are required for our studies. Several publications [20 to 22] have dealt with crude oil separations by the HPLC method. In our work, only deasphaltenated maltene could be analyzed by this method. Use was made of an HPLC instrument made by Waters Associates (prepak-NH_2, P/N 10008

columns), and n-heptane (HPLC grade from Fisher Scientific) was used as the mobile phase. By the use of this method aromatics were separated partially into further fractions, depending on the number of condensed rings in the molecule. However, this method was not used to any extent as it was less suitable for the present studies than the ASTM methods.

No attempt was made to separate further the saturated fraction into naphthenes and paraffins; the later studies showed that such a separation would not be of any value.

ANALYSES

Speight [1] and Uden et al. [23] have described in detail various analyses of petroleums and related materials. Several procedures have been used in the present work. A number of workers [24 to 29] have used infrared (IR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy to determine different functional groups in bitumens. In the present work these two techniques, and also elemental analysis, have been used to characterize the fractions obtained by the chromatographic procedures.

NMR Spectroscopy

The 1H FTNMR and 13C FTNMR spectra, in $CDCl_3$ solution, were taken with the asphaltene fractions of Cold Lake bitumen, and the results are shown in Figures 3 and 4. Detailed FTNMR studies were not made, since it was not considered that they would provide additional information.

Structural studies of the bitumen fractions were carried out using 1H NMR spectroscopy, all of the spectra being taken in $CDCl_3$ solution. Some typical spectra are shown in Figures A1 to A8; the same fractions from different bitumen sources showed very similar spectra.

The NMR spectra of the fractions show a strong band near 7.2 δ (Figure 3); this corresponds to aromatic hydrogen atoms. This band is absent from the spectra obtained from the saturated fraction (Figure A1), showing that a good separation of aromatics has been achieved. The sharp bands between 1 and 2 δ are due to aliphatic protons. The signal at 0.9 δ shows paraffinic methyl protons, whereas that at 1.35 δ is due to protons from methylene groups. The signal in the 1.8 to 2.2 δ region may be due to naphthenic protons; these bands are present

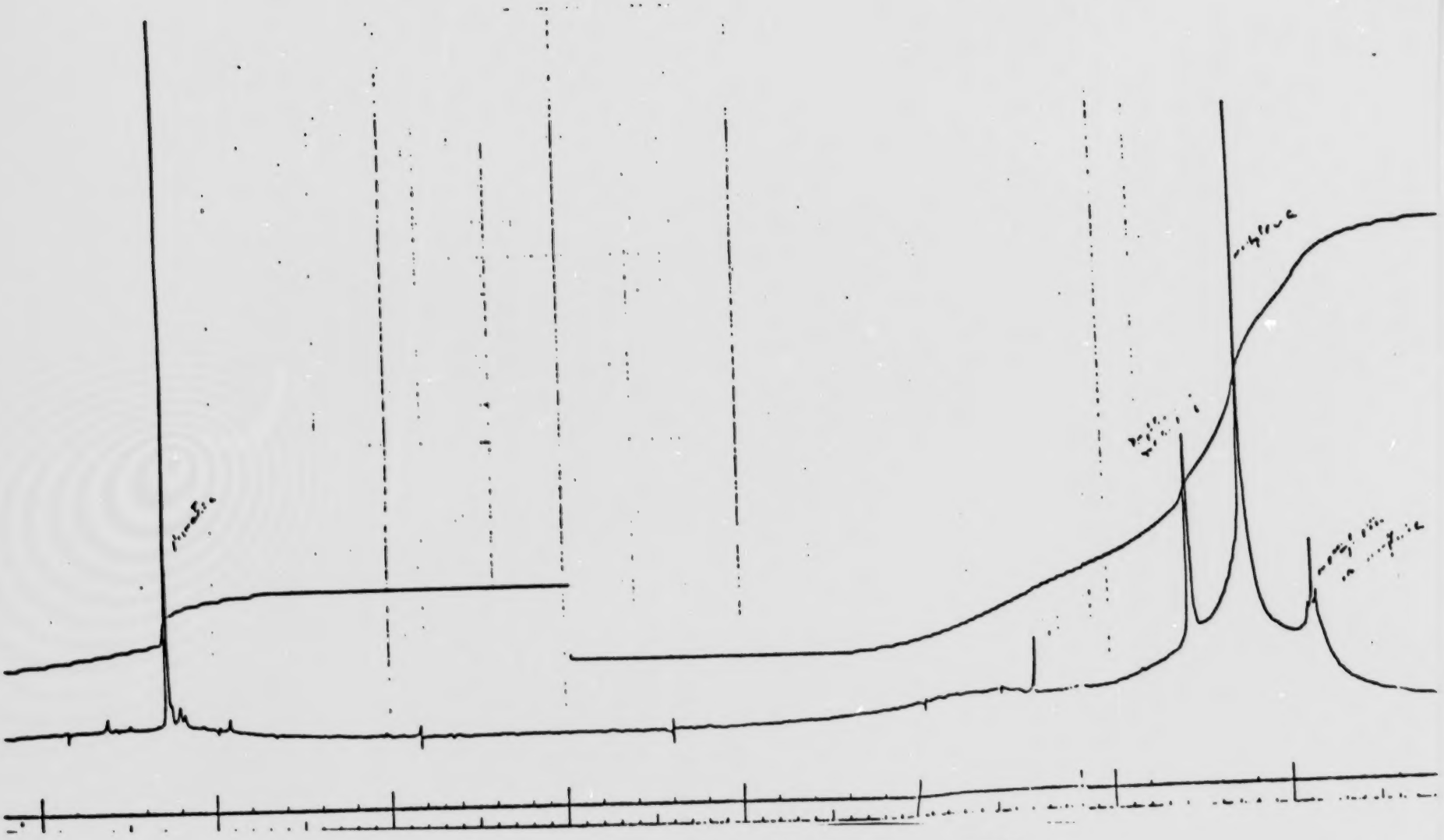


Figure 3. 1H FTNMR spectra of the asphaltene from Cold Lake bitumen in $CDCl_3$

Spectral lines for Fig. 4

XL-300 13C OBSERVE
SPECTRAL LINES FOR TH= 20.00
REL= 6755.7 REF= 5008.0

INDEX	FREQ	PPM	INTENSITY
01	9731.1	129.010	30.868
02	9670.1	128.202	30.628
03	9419.6	125.277	23.422
04	5863.4	77.734	135.124
05	5855.3	77.627	61.256
06	5839.7	77.420	2.18E 3
07	5823.1	77.200	132.242
08	5807.5	76.993	2.20E 3
09	5775.7	76.572	2.18E 3
10	5751.1	76.245	120.110
11	5733.4	76.011	20.539
12	5726.4	75.918	23.181
13	5710.8	75.711	23.422
14	2573.3	34.116	22.341
15	2407.6	31.919	27.505
16	2289.8	30.357	20.299
17	2284.2	30.283	22.341
18	2279.2	30.217	25.944
19	2264.1	30.016	43.480
20	2240.4	29.703	156.744
21	2225.8	29.509	38.916
22	2215.3	29.369	37.997
23	1711.6	22.692	33.391
24	1685.0	22.338	32.790
25	1044.5	13.113	33.071
26	1041.5	13.073	33.035

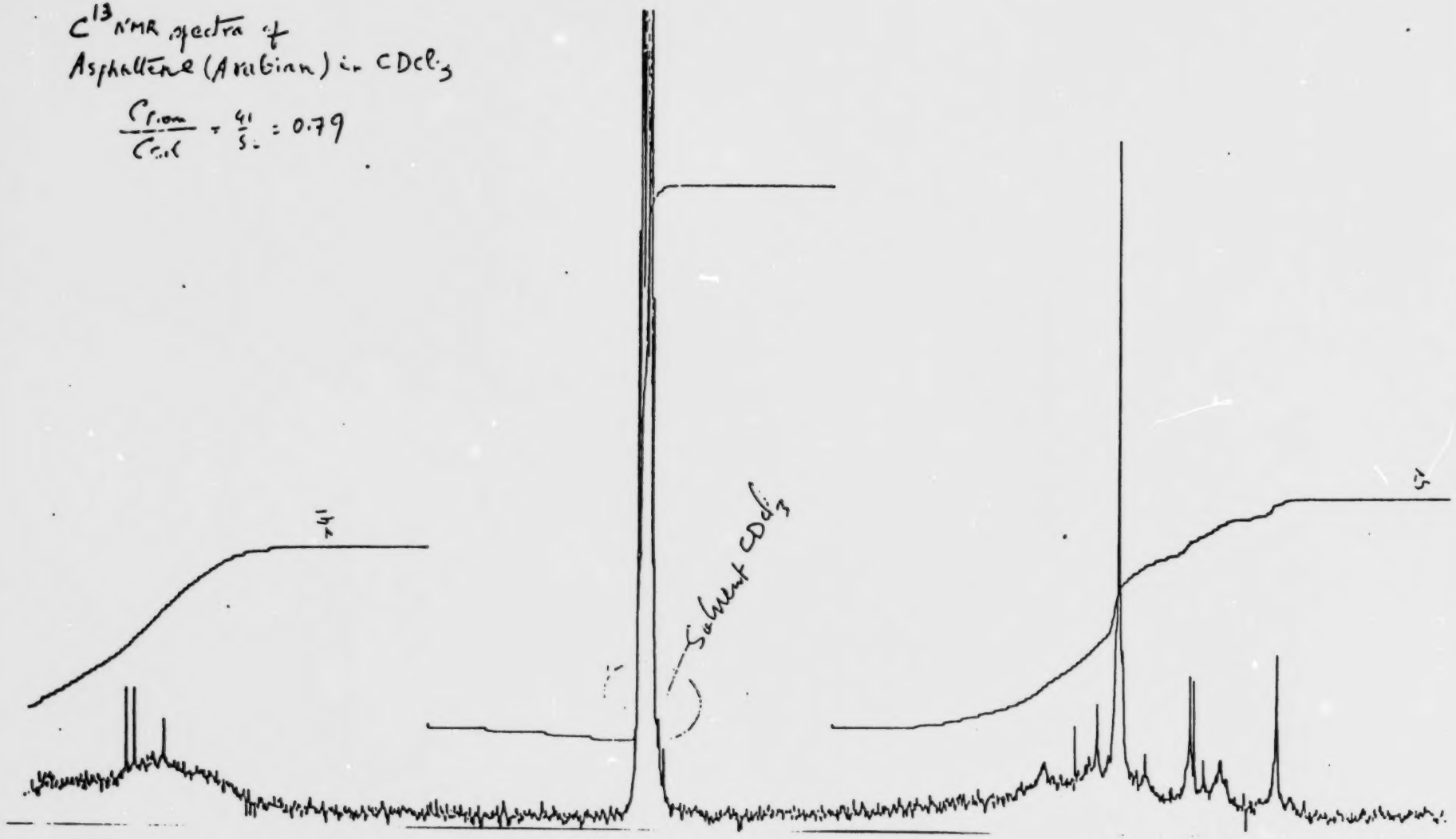


Figure 4. 13C FTNMR spectra of the asphaltene from Cold Lake bitumen in $CDCl_3$

in the aromatic fraction as well as the saturated fraction. The bands in the aromatic fractions are due to aliphatic side chains. The signal near 2.5 δ, present only in the aromatic fraction, is due to the methyl group attached to the aromatic rings.

Additional NMR spectra are shown in the Appendix [Figures A1-A8].

Figures A7 and A8 show NMR spectra of the hard and soft resins. They indicate that these resins have some aromatic structure as well as some naphthenic and paraffinic groups. There are some additional bands due to protons adjacent to the hetero groups. The signal around 2.5 δ may be due to ketonic groups. Peaks at 4 δ and 6 δ may also be due to the protons of amine and hydroxyl groups. Hard resins have more signals due to protonic groups adjacent to heteroatoms, as compared with soft resins.

Infrared Spectroscopy

IR spectra were taken in carbon tetrachloride solution, and typical spectra of different fractions from Arabian bitumen are shown in Figures 5 to 9. Additional spectra are shown in the Appendix [Figures A9-A12].

The IR spectra provide important information about some functional groups. Strong bands at 1600 cm^{-1} and 800 cm^{-1} indicate the $-CH_2-$ group in a cyclic structure. A broad band near 3500 to 3000 cm^{-1} is due to a hydrogen-bonded OH or NH group. This is practically absent in hard resin. The 1660 cm^{-1} band in the soft resin represents a free CO group which is absent in the hard resin. Both samples show bands in the region 1300-1200 cm^{-1}, indicating oxygen present in an ether linkage between two aromatic rings. The band in the region 1600-1500 cm^{-1} suggests nitrogen in the form of amide. The sharp band near 1000 cm^{-1} may be due to sulfur present in S = O.

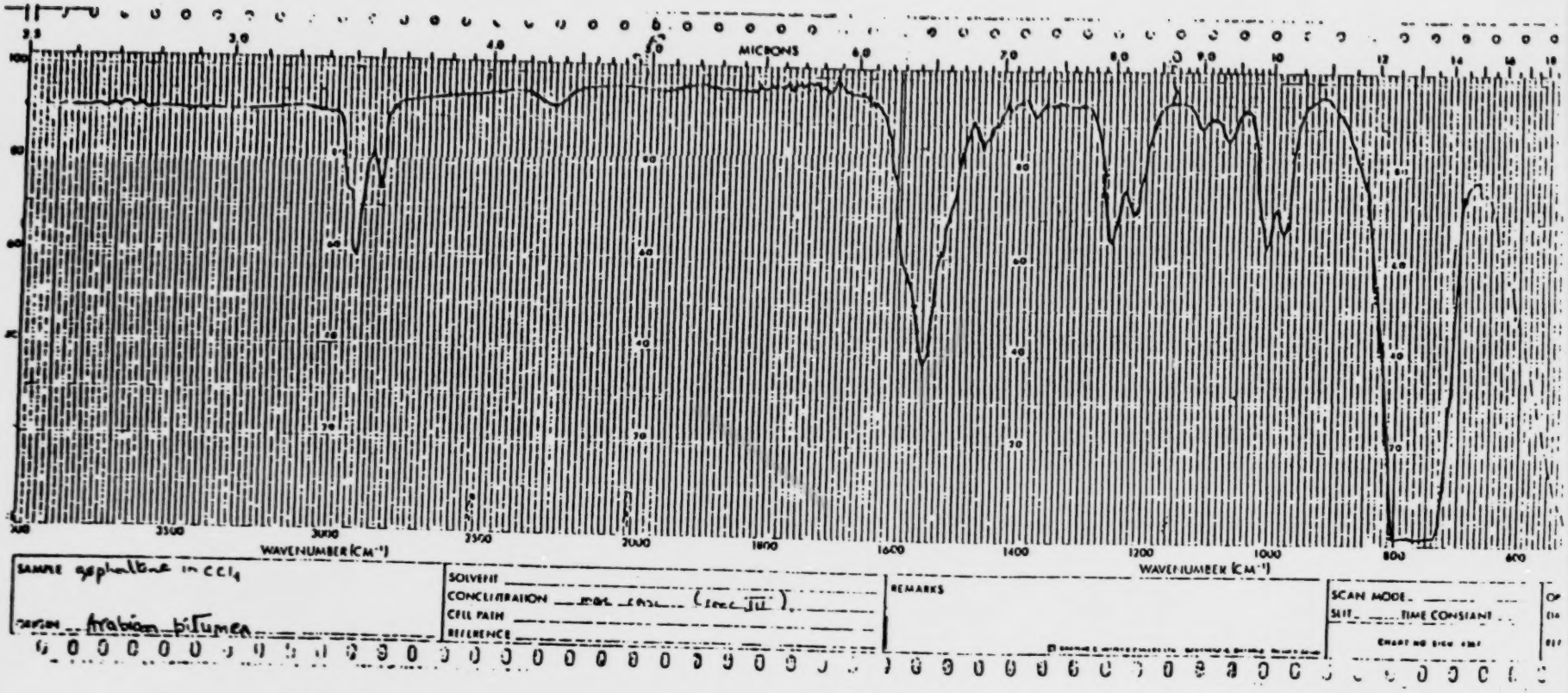


Fig. 5 - IR spectra of the asphaltenes from Arabian bitumen in CCl_4

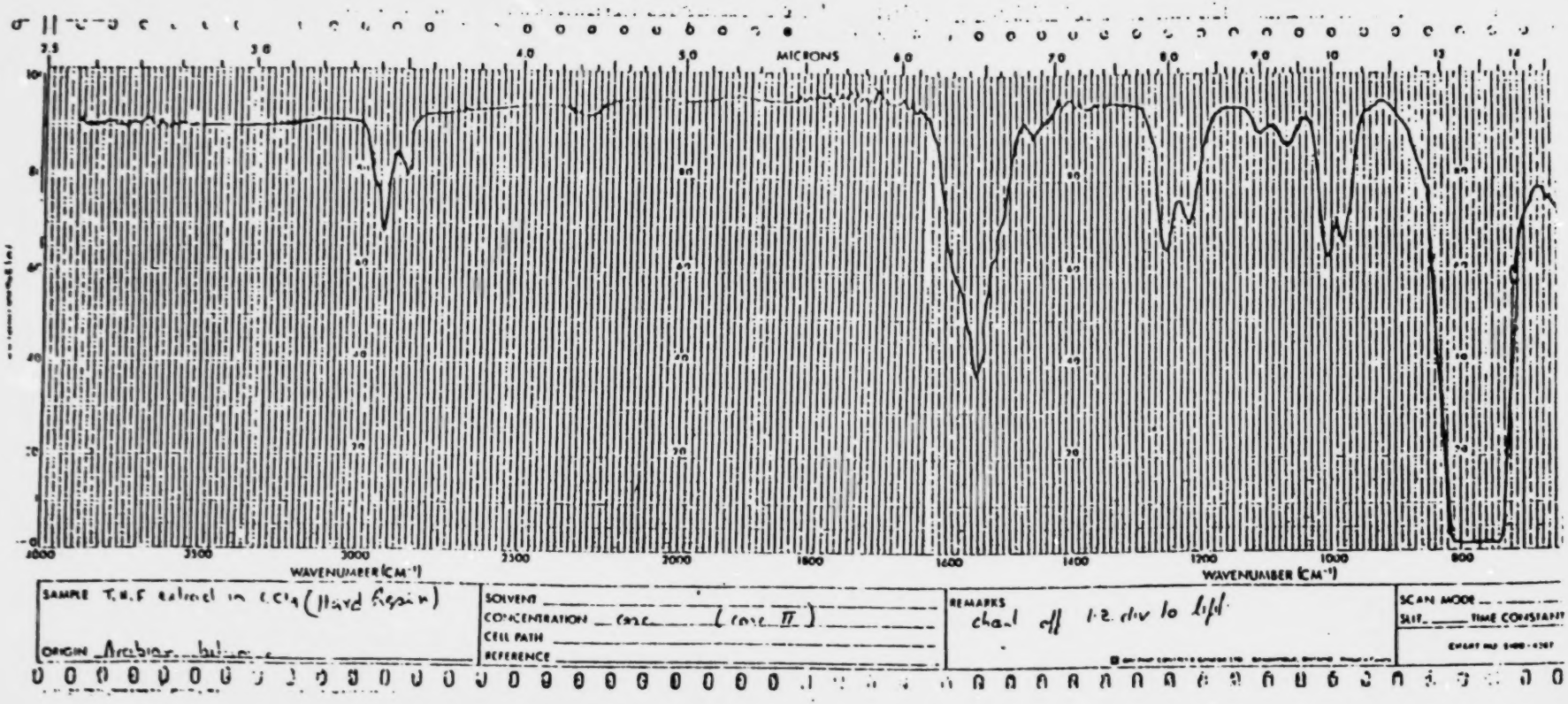


Fig. 6 - IR spectra of the hard resin from Arabian bitumen in CCl_4

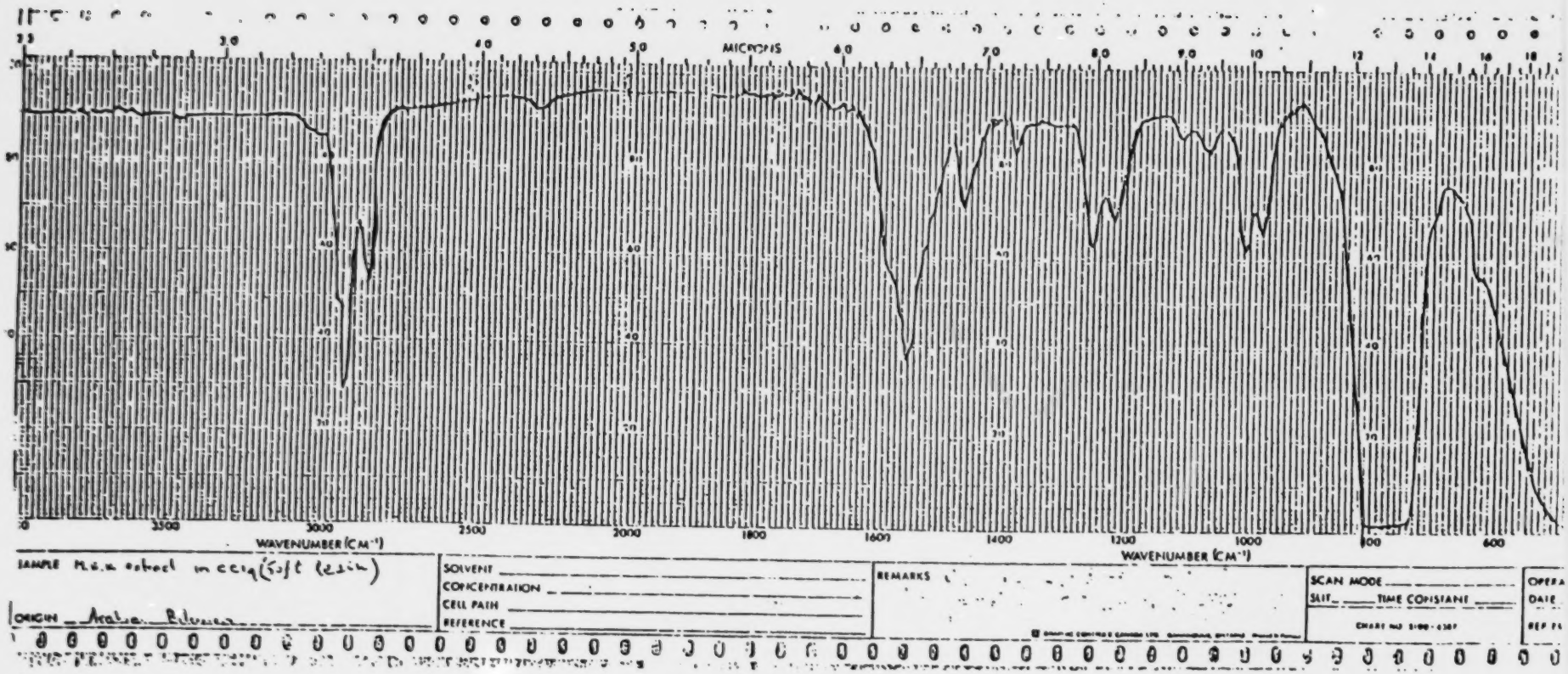


Fig. 7 - IR spectra of the soft resin from Arabian bitumen in CCl_4

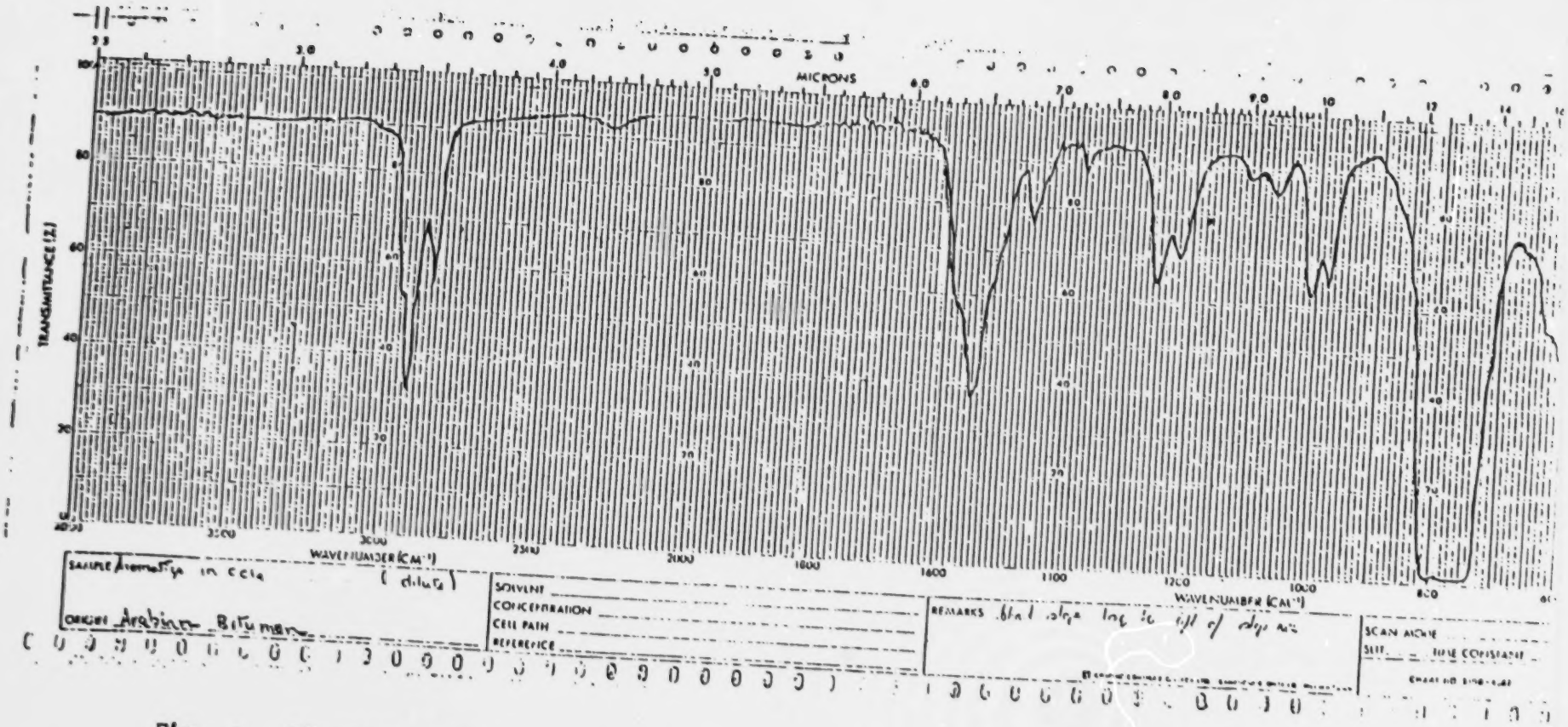


Fig. 8 - IR spectra of the aromatics from Arabian bitumen in CCl_4

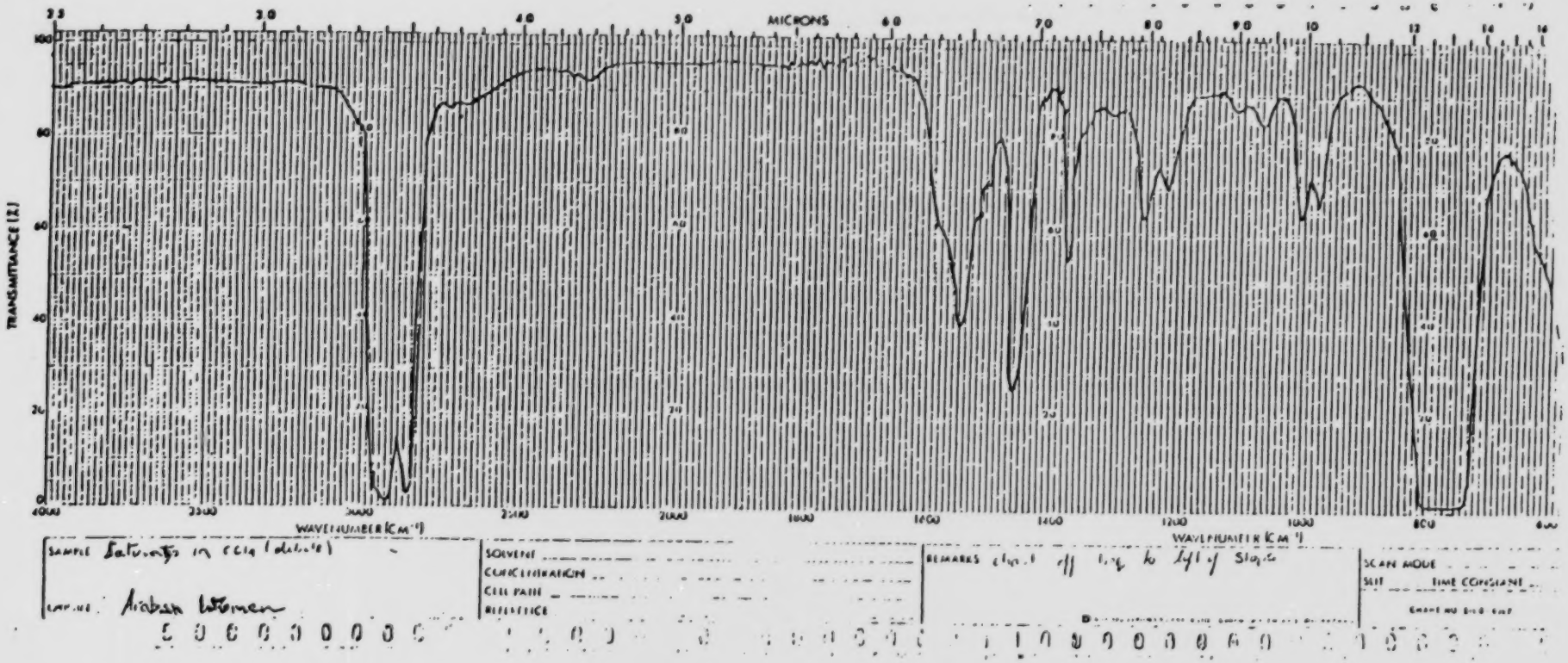


Fig. 9 - IR spectra of the saturates from Arabian bitumen in CCl_4

Elemental Analysis

The elemental analyses of the bitumens were carried out by CANMET, and the results supplied by them are reproduced in Table 1.

The elemental analyses for the fractions separated from the bitumens were done by Microanalytical Laboratories, Vancouver, B.C. Their results are presented in Table 3.

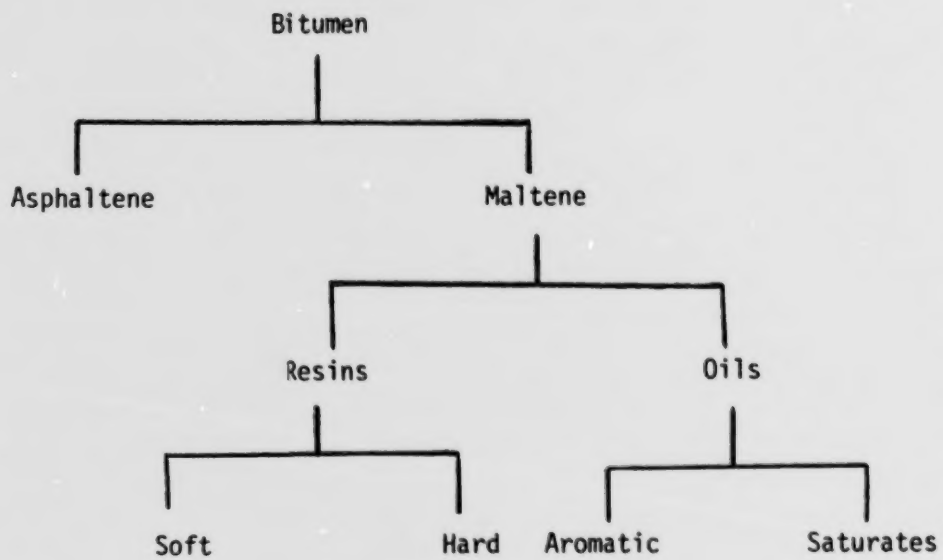
Table 3

Elemental analyses of the bitumen fractions (wt%)

	Asphaltene	Soft resin	Hard resin	Aromatics	Saturates
Cold Lake					
C	81.64	82.07	81.22	87.12	86.56
H	8.03	9.43	9.05	11.03	13.38
N	1.25	0.93	0.94		
O	1.10	1.38	2.93		
S	7.97	5.90	4.92		
H/C	1.18	1.38	1.33	1.52	1.85
N/C	0.013	0.009	0.009		
O/C	0.010	0.013	0.027		
S/C	0.037	0.027	0.023		
Arabian					
C	84.04	83.97	83.56	87.03	86.05
H	7.74	8.86	8.93	11.06	14.07
N	1.04	0.89	0.78		
O	0.86	1.81	2.23		
S	6.40	5.15	3.49		
H/C	1.11	1.26	1.28	1.53	1.96
N/C	0.010	0.009	0.008		
O/C	0.007	0.016	0.020		
S/C	0.028	0.023	0.015		

DISCUSSION

The bitumens were separated into several compounds according to the following scheme:



The relative percentage of the components are calculated and presented in Table 2. Cold Lake bitumen contains a much greater quantity (24.4 %) of asphaltene than the Arabian fraction (15.9 %).

It has been observed that the total resin content is lower in Cold Lake bitumen (26.8 %) than in Arabian (28.5 %). In all of the cases soft resin is present at a much higher percentage than the hard resin. The aromatic content is almost the same in both the bitumens. Saturated hydrocarbons are present in much lower quantity (15.9 %) in the Cold Lake bitumen as compared to the Arabian (22.3 %).

The results of the analyses of the bitumens, presented in Table 1, show that Arabian bitumen has a higher API gravity (6.82) than the Cold Lake bitumen (4.95). Cold Lake bitumen is sulfur-rich (5.9 %), whereas Arabian bitumen has a lower proportion of sulfur (4.5 %).

Elemental analyses show that the H/C ratio is low for Arabian bitumen (1.39) as compared to Cold Lake (1.44), and this shows that Arabian bitumen is more aromatic. Arabian bitumen is low in nitrogen (0.2%) as compared to Cold Lake (0.4%). It was observed that both the bitumens have a very low percentage of ash content (0.01%), and of inorganic elements. A similar result was found for the toluene-insoluble portion.

Elemental analyses of all the fractions were carried out, and the results are presented in Table 3. The H/C ratios indicate in an inverse way the aromaticities of the fractions. It was observed that asphaltene has the highest aromaticity of all the fractions in each bitumen. Comparison of different asphaltenes shows that Arabian has a higher aromaticity (H/C = 1.11) than Cold Lake (H/C = 1.18).

Resin is the next most aromatic compound present in the bitumen. Its aromaticity value is lower than that of asphaltene but higher than that of pure aromatic compounds. It was found that the aromaticities of the resins of Arabian bitumen are higher (H/C = 1.2) than for Cold Lake (H/C = 1.3). It is also interesting to observe that both the soft and hard resins have almost the same H/C value. The atomic ratios of the elements nitrogen, oxygen and sulfur with respect to carbon, do not change much as the source of the resins is changed.

The H/C ratios of the aromatics are almost the same for both the sources, but the H/C ratios of the saturates are different. The saturated fraction of Arabian bitumen is more hydrogenated (H/C = 1.96) than that of the Cold Lake fraction (H/C = 1.85).

The atomic ratios of the hetero atoms with respect to carbon atoms show that sulfur is present in highest quantity in asphaltenes and resins, followed by oxygen and nitrogen. Although both the resins contain almost the same quantity of nitrogen, the hard resin contains more oxygen and less sulfur as compared to soft resin. The saturated fraction was found to be almost free of hetero atoms.

Part II KINETICS OF THE PYROLYSIS OF BITUMEN FRACTIONS IN THE PRESENCE OF SULFUR

In investigations described previously (9,10,11), bitumen fractions were pyrolyzed in an atmosphere of nitrogen. The present section describes kinetic studies of the pyrolyzes in the presence of various amounts of sulfur, also carried out in an inert atmosphere. The work was done with asphaltene and hard and soft resins from Cold Lake bitumen.

Experimental

The bitumen fractions were supported in a quartz crucible, and various amounts of pure sulfur were added. Pyrolysis was brought about at temperatures of 400° to 440°C, at contact times ranging from 3 minutes to 15 minutes. The work was done in a special temperature-controlled furnace, supplied by Lindberg of Wisconsin. The furnace was modified so as to allow the quartz crucible to be hung inside it, and also to allow dry nitrogen to be passed through the system. The furnace could be programmed for a given temperature range at a given rate of heating; the temperature could be held constant for a certain time, and then could be cooled rapidly.

In all of the experiments the reactions were carried out in dry oxygen-free nitrogen, which was passed at a constant rate through the reaction system. After the sample had been held for a known period of time at a predetermined temperature, it was taken out of the furnace and cooled rapidly to room temperature by blowing nitrogen through it; this minimized secondary reactions. The residue formed in the crucible was weighed and then extracted with toluene and filtered. The residue that was insoluble in toluene was then weighed.

Results

The results are given in Table 4, and some of them are presented graphically in Figures 10 to 13. The main features of the results are as follows:

(1) With the asphaltene at temperatures above 400°C, all of the residue was insoluble in toluene. This was not the case with the pyrolysis in the absence of sulfur (9), where some of the residue was soluble in toluene.

(2) With asphaltene pyrolyzed at 400°C, increasing the reaction time from 5 min. to 10 min. has little effect on the amounts of residue formed. This is shown clearly in Figure 10. Increasing the temperature from 400° to 420°C slightly increases the amounts of residue (Figure 12). However, a further rise of temperature to 440°C has little effect on the amounts of residue (Figure 12).

(3) With asphaltene pyrolyzed at 400°C, addition of small amounts of sulfur brings about a considerable increase in the amount of toluene-insoluble residue, as shown in Figure 10. The addition of further amounts has a much smaller effect.

(4) With asphaltene pyrolyzed at over 400°C, addition of sulfur decreased the total amount of residue formed, but increased the amount of toluene-insoluble residue.

(5) With asphaltene pyrolyzed at 380°C the results are quite different. As the amount of sulfur was increased the amount of coke formed passed through a minimum. Thus at this temperature small amounts of sulfur caused a decrease in the coke formation.

(6) When soft resin was pyrolyzed with sulfur at temperatures above 420°C, the residue was completely insoluble in toluene (Table 4). The same was true

Table -4

Pyrolysis of Cold Lake bitumen fractions with Sulfur

Exp No.	Temp./°C	Time/min.	wt% Sulfur	wt% Residue	wt% Toluene-insoluble residue
Asphaltene					
51	380	5	2.7	84.2	11.5
52	380	5	3.8	83.3	13.9
53	380	5	5.2	81.1	17.3
54	380	5	6.4	73.0	21.2
55	380	5	8.4	62.7	26.3
56	380	5	Nil	67.8	21.8
57	400	3	5.5	45.1	45.1
58	400	5	2.6	47.2	47.2
59	400	5	3.9	49.4	49.4
60	400	5	5.6	50.7	50.7
61	400	5	13.5	52.4	52.4
62	400	5	27.1	53.8	53.8
63	400	5	Nil	65.5	23.6
64	400	7	5.4	50.9	50.9
65	400	10	5.1	51.5	51.5
66	400	10	8.3	54.1	54.1
67	400	10	Nil	58.7	35.5
68	420	5	5.8	56.1	56.1
69	440	5	5.3	56.9	56.9

Table 4 Cont.

Cont. Table 4

Exp. No.	Temp./°C	Time/min.	wt% Sulfur	wt% Residue	wt% Toluene insoluble residue
Soft resin					
70	400	5	2.8	26.6	10.8
71	400	5	3.7	24.2	12.2
72	400	5	5.9	21.6	15.4
73	400	5	8.1	20.1	15.8
74	400	5	Nil	55.5	16.6
75	420	3	5.4	22.8	20.8
76	420	5	2.3	31.1	31.1
77	420	5	3.4	31.9	31.9
78	420	5	4.6	32.5	32.5
79	420	5	5.6	32.8	32.8
80	420	5	Nil	37.8	22.2
81	420	7	5.5	34.9	34.9
82	420	10	5.4	35.0	35.0
83	440	5	5.4	34.4	34.4
Hard resin					
84	400	5	5.4	29.9	29.9
85	420	3	5.5	30.9	30.9
86	420	5	5.4	41.5	41.5
87	420	7	5.5	42.8	42.8
88	420	10	5.6	43.3	43.3
89	420	5	2.2	33.3	33.3
90	420	5	3.5	38.2	38.2
91	420	5	7.8	41.9	41.9
92	420	5	Nil	44.8	23.8
93	440	5	5.4	44.4	44.4

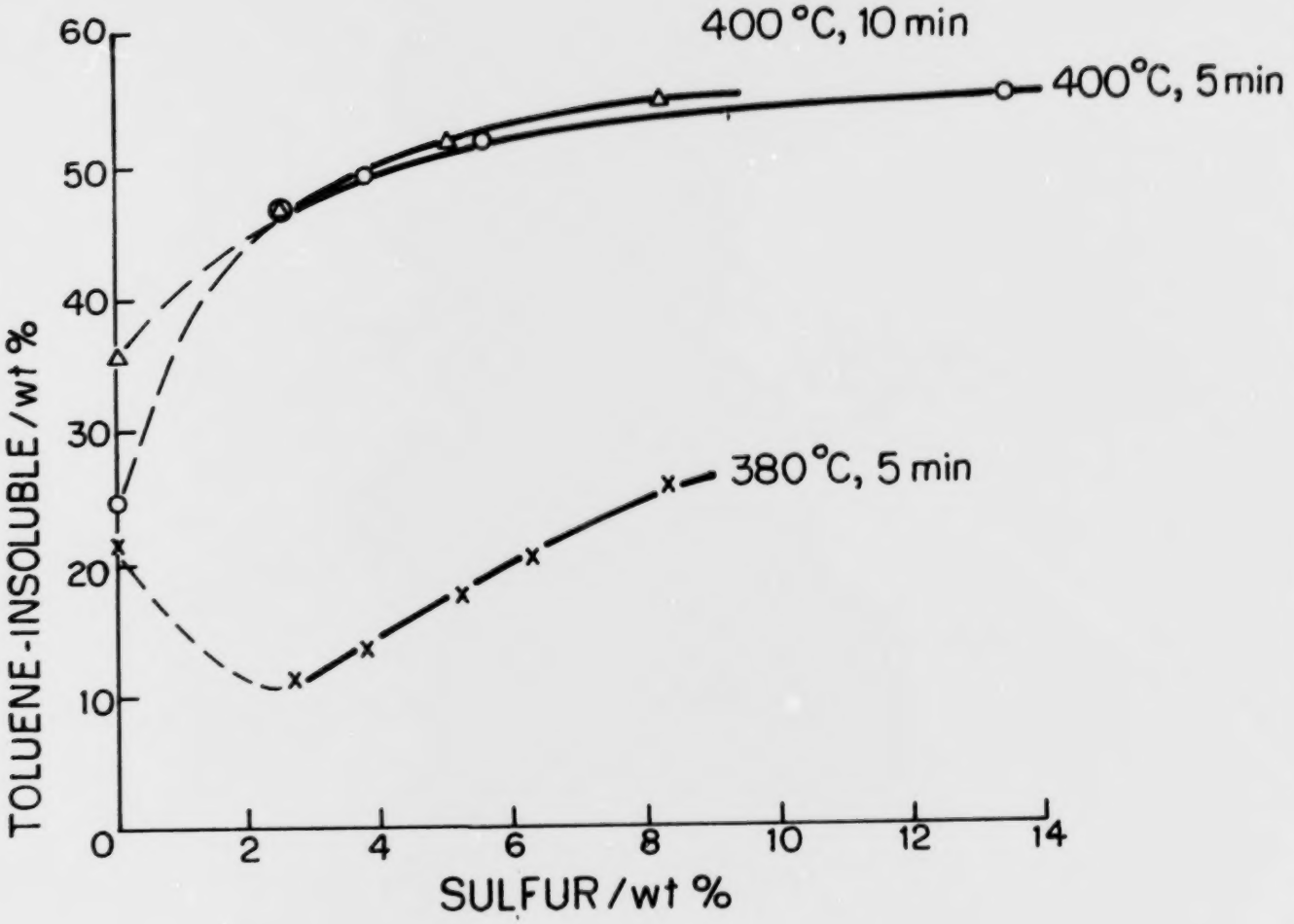


Figure 10. Variation of Toluene-insoluble with the amount of Sulfur for Cold Lake asphaltene; temperatures and times as indicated.

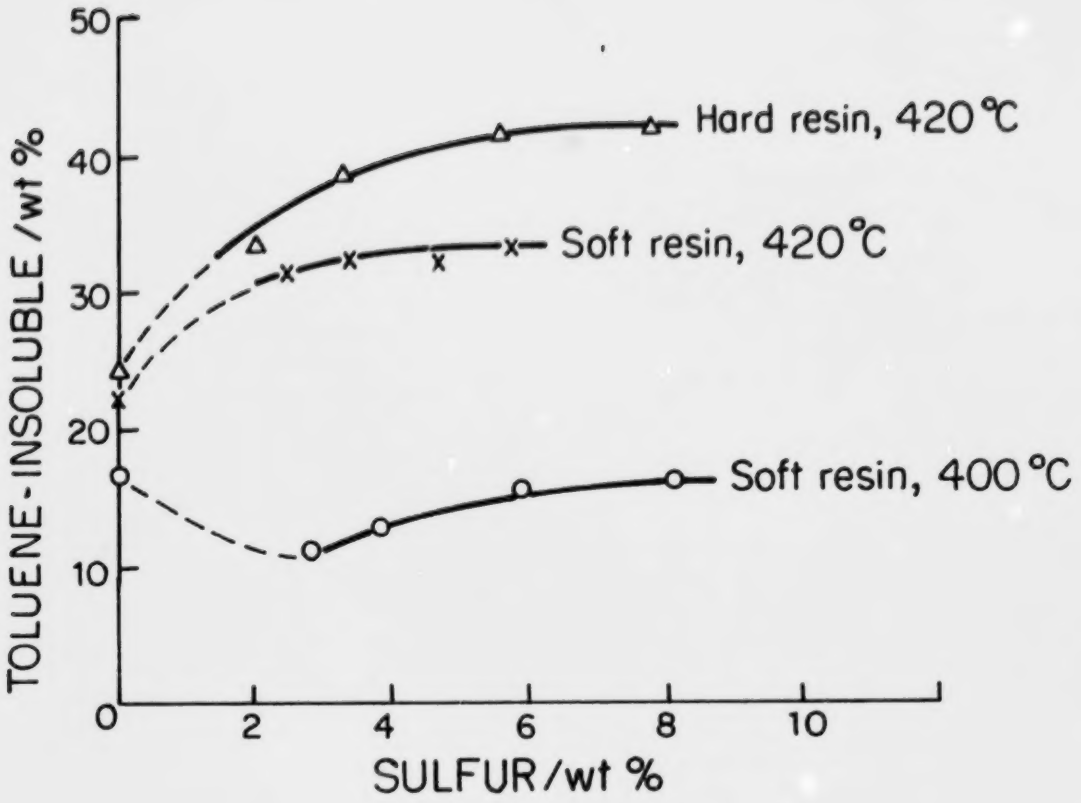


Figure 11 . Variation of Toluene-insoluble with the amount of Sulfur for Cold Lake resins after 5 minutes; temperatures as indicated.

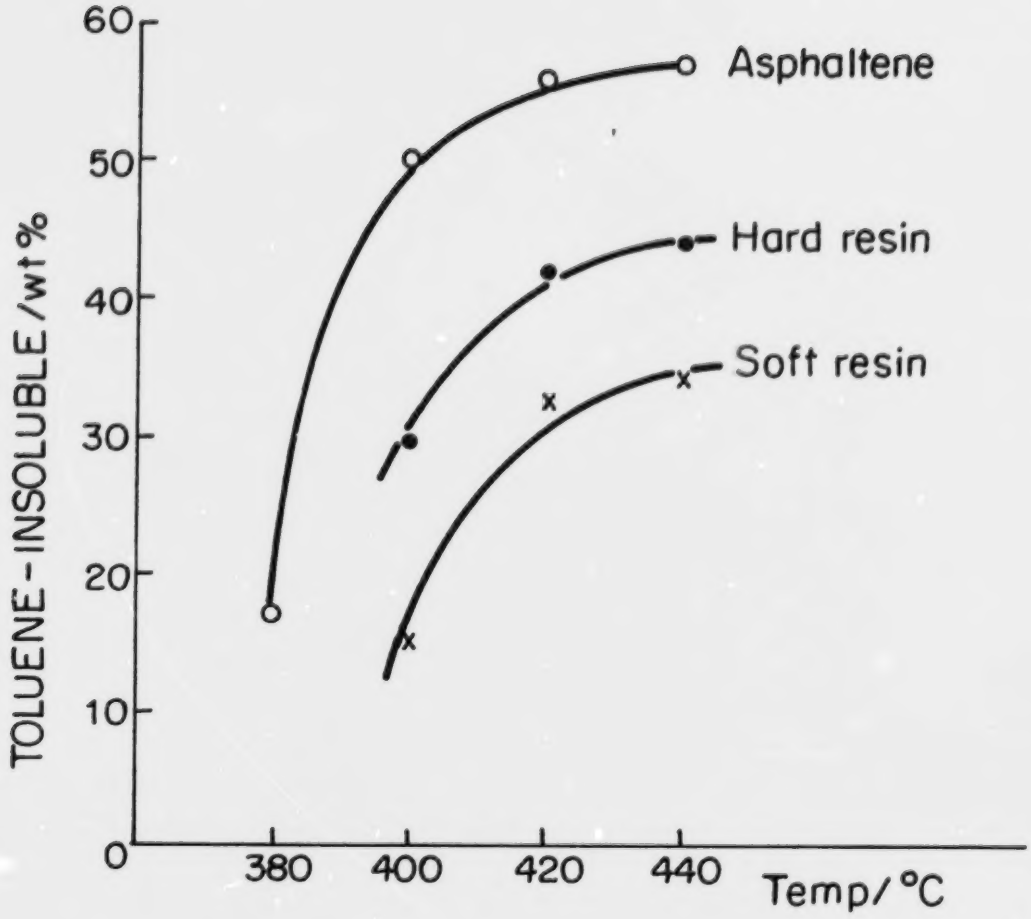


Figure 12. Variation of Toluene-insoluble with temperatures for Cold Lake fractions, after 5 minutes.
Sulfur= 5.5 wt%.

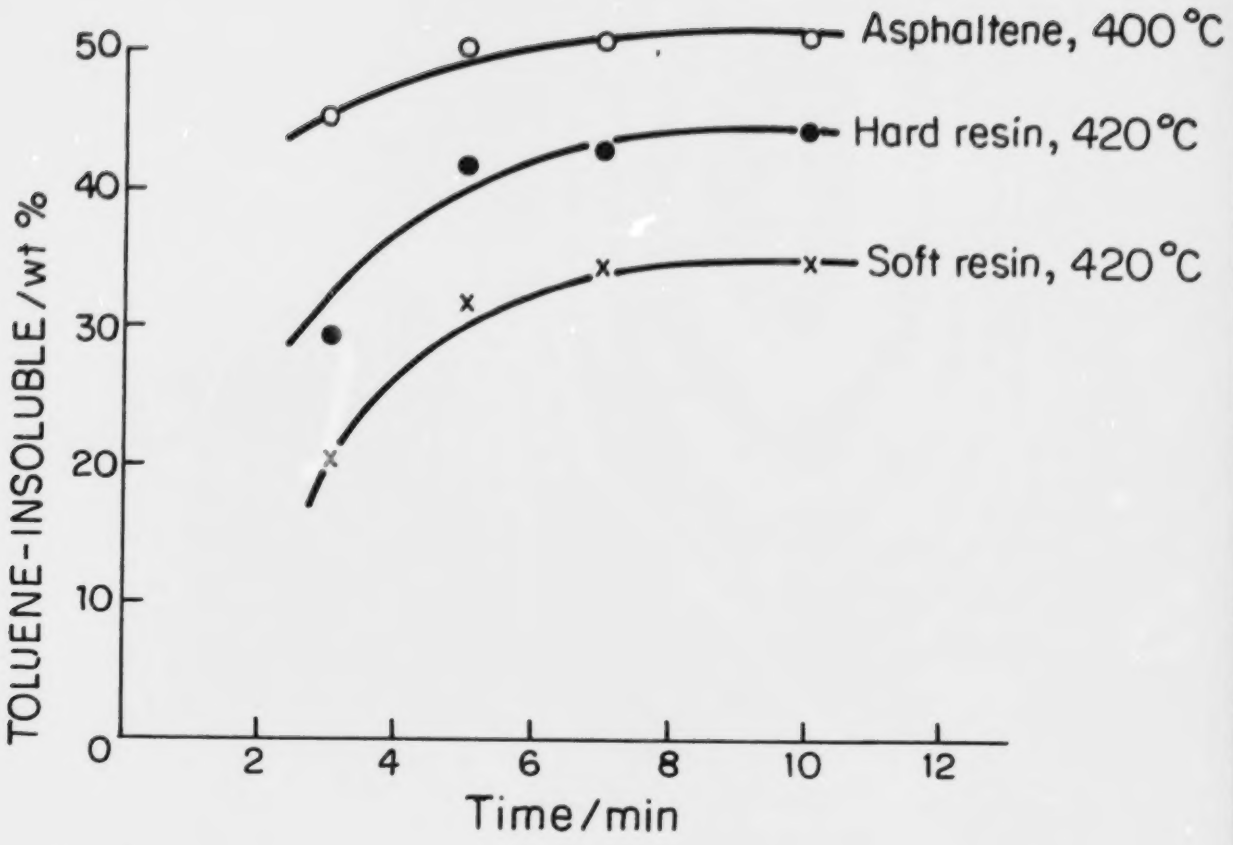


Figure 13. Variation of Toluene-insoluble with Times for Cold Lake fractions; temperatures as indicated.
Sulfur = 5.5 wt%.

with hard resin at temperatures from 400°C to 440°C. With soft resin at lower temperatures the residue was only partly insoluble in toluene.

(7) When pyrolyzed with sulfur, hard resin always gave 5-10% more toluene-insoluble residue than soft resin. This is in contrast to the situation in the absence of sulfur (9), where both types of resin produced essentially the same amounts of toluene-insoluble residue.

(8) With soft resin pyrolyzed at 400°C, addition of sulfur decreases the total amount of residue formed, but increases the amount of toluene-insoluble residue.

(9) With all three fractions, asphaltene, hard resin, and soft resin, the amount of toluene-insoluble residue appears to reach a limiting value after about 5 min. contact time, and does not appear to continue to increase with temperature after about 420°C.

Discussion

Some previous investigations throw some light on the present results. Thus Cellet [30] and Didchenka [31] made thermal studies on pitches with the addition of sulfur, and found discontinuities in the viscosity-temperature behavior. Balduhn [32] found evidence that the addition of sulfur to pitch produces cross linkages in the form of polysulfide bridges, which are preserved even up to temperatures of 1450°C.

These results and those of the present investigation suggest that sulfur suppresses coke formation by bringing about an alternative process in which cross-linking takes place; this leads to a hardened product which is insoluble in toluene and which is therefore coke according to the present definition.

The dark-colored residue obtained in the present investigations with sulfur was a single piece of solid material which did not stick to the walls of the quartz boat. In the absence of sulfur the coke formed sticks to the wall. This is consistent with the fact that much of the residue formed in the presence of sulfur is not a coke, but has been produced as a result of cross-linking of the sulfur with the free-radical intermediates formed in the thermal cracking processes. This product is of higher molecular weight, but is not a coke.

The main practical conclusion from the present work is that sulfur is most effective as a suppressor of coke formation if it is used in small amounts at lower temperatures, such as 380^{o}C. At higher temperatures and in larger amounts sulfur tends to increase coke formation.

PART III KINETICS OF COKE FORMATION FROM FRACTIONS OF ARABIAN AND COLD LAKE BITUMEN UNDER HYDROGEN

The object of the work to be described was to study the kinetics of coke formation from different fractions of bitumens, under an atmosphere of hydrogen. By determining energies of activation for the different processes it was hoped to gain some insight into the mechanisms of coke formation under these conditions, with a view to bringing about some reduction.

Experimental

The compounds were hydrocracked in a batch system. A specially designed hydrocracking unit was used for the purpose. The micro-reactor was a stainless steel autoclave of volume 15 cm^3, which was capable of operation at a hydrogen pressure of up to 30 MPa and at temperatures up to 500^oC. One thermocouple was inserted into the salt bath to control the temperature of the heating system, and another thermocouple was inserted into the thermowell of the micro-reactor to measure the temperature of the reaction mixture.

The sample was thoroughly mixed with hydrogen with the help of an up-and-down agitating system. The reactor was mounted in a handle, connected to a motor with a variable speed control. The agitating speed was kept constant at 800 strokes per minute for all the experiments.

The reactor was heated to the required temperature by raising a pre-heated salt bath up to the reactor, with the help of a hydraulic pump. The contents of the reactor rapidly come to the required temperature, reaching 450^oC within 3 minutes. The agitation of the reactor in the salt bath caused the heating to be uniform throughout the system.

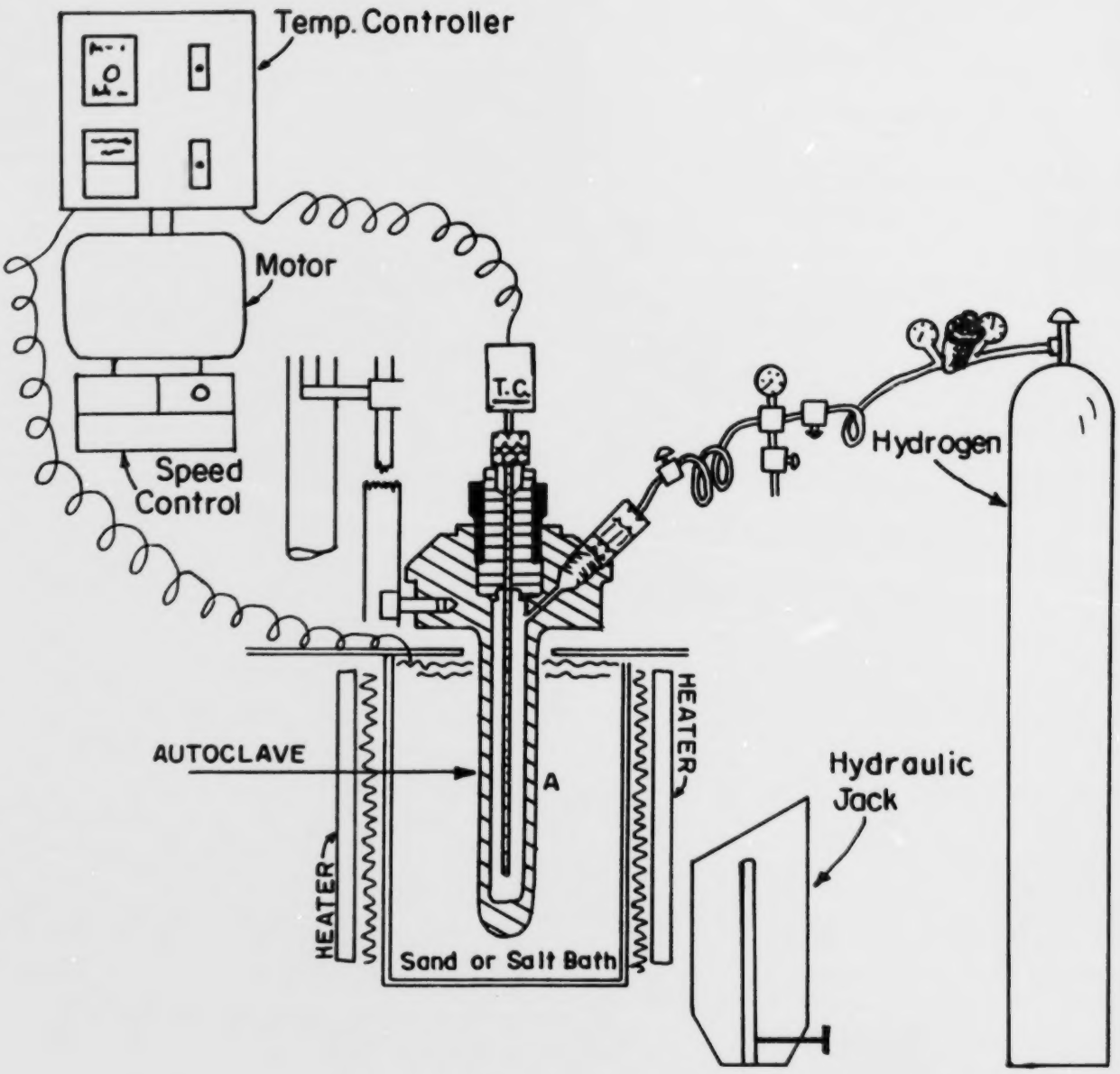


Diagram of Hydrocracking Unit

About 1 g of the sample was introduced into the reactor for each reaction. The reactor was the pressurized with hydrogen to the required pressure (usually 15 MPa), and sealed completely by closing the valves. Hydrogen leakage was checked with the help of soap solution. The system was agitated for some time, before being placed in the salt bath, and it was further agitated in the salt bath at the predetermined temperature.

At the conclusion of the reaction period the reactor was rapidly cooled (within 2 minutes) to room temperature by replacing the salt bath with a water bath and passing cold water through the system. The reactor was then vented, and the contents carefully removed by toluene extraction. The toluene extract was filtered in a weighed sintered crucible by means of a vacuum pump.

The crucible and the reactor were both washed with toluene and dried in an oven at 120^{o}C for some time, then weighed to determine the amount of coke formed. Each experiment was repeated at least 3 times and the reproducibility of these results was within ± 3 wt%.

Results

The amounts of coke formed, with respect to the feed, from different fractions of Cold Lake bitumens are listed in Table 5, and for Arabian fractions in Table 6. The variations in coke formation as a function of time and temperature for the various fractions are shown in Figures 14 to 22. The total amount of residue obtained was 93-96% of the feed; the rest consisted of volatile products.

Table 5

Kinetic results for coke formation: Cold Lake fractions

Compound	Exp. No.	H_2 pressure /MPa	Temp./^oC	Time/min	Coke/wt%
Asphaltene					
	94	15	380	20	7.1
	95	15	380	30	10.7
	96	15	380	45	14.8
	97	15	380	60	16.1
	98	15	400	20	11.6
	99	15	400	30	15.0
	100	15	400	45	18.2
	101	15	400	60	20.2
	102	15	420	20	16.0
	103	15	420	30	21.1
	104	15	420	45	24.8
	105	15	420	60	25.6
	106	15	440	20	20.7
	107	15	440	30	27.3
	108	15	440	45	28.1
	109	10	400	30	14.7
	110	20	400	30	15.1
Hard resin					
	111	15	380	30	3.1
	112	15	400	20	4.1
	113	15	400	30	6.3
	114	15	400	45	9.0
	115	15	400	60	11.1
	116	15	420	20	7.2
	117	15	420	30	11.2
	118	15	420	45	14.1
	119	15	420	60	14.9
	120	15	440	20	9.8
	121	15	440	30	13.2
	122	15	440	45	18.4
	123	15	440	60	19.7
	124	15	460	20	12.1
	125	15	460	30	17.0
	126	15	460	45	19.9

Continued

Table 5 (Continued)

Compound	Exp. No.	H_2 pressure/MPa	Temp/^{o}C	Time/min	Coke/wt%
Soft Resin	127	15	380	30	3.0
	128	15	400	20	3.3
	129	15	400	30	5.2
	130	15	400	45	6.9
	131	15	400	60	8.4
	132	15	420	20	4.1
	133	15	420	30	6.8
	134	15	420	45	8.6
	135	15	420	60	9.5
	136	15	440	20	5.4
	137	15	440	30	8.8
	138	15	440	45	9.8
	139	15	440	60	10.9
	140	15	460	20	8.2
	141	15	460	30	12.1
	142	15	460	45	14.8
	143	15	460	60	15.9
	144	10	440	30	8.01
	145	20	440	30	8.61
Aromatics	146	15	440	30	no coke
	147	15	460	30	no coke
	148	15	440	60	0.5
	149	15	460	60	1.5
	150	15	480	30	3.6
	151	15	480	45	4.6
	152	15	480	60	7.1
Bitumen	153	15	380	30	5.2
	154	15	400	20	7.7
	155	15	400	30	10.4
	156	15	400	45	13.8
	157	15	400	60	15.1
	158	15	420	30	14.5
	159	15	440	30	16.7

Table 6

Kinetic results for coke formation: Arabian bitumen fractions

Compounds	Exp. No.	H_2 pressure/MPa	Temp./^{o}C	Time/min.	Coke/wt%
Asphaltene	160	15	380	15	12.4
	162	15	380	30	19.3
	163	15	380	45	22.8
	164	15	380	60	25.1
	165	15	400	15	19.2
	166	15	400	30	28.9
	167	15	400	45	35.1
	168	15	400	60	36.2
	169	15	420	15	21.7
	170	15	420	30	35.6
	171	15	420	45	37.2
	172	15	440	15	24.0
	173	15	440	30	37.3
	174	15	440	45	37.7
	175	10	440	30	37.5
	176	20	440	30	36.8
Hard resin	177	15	380	30	no coke
	178	15	380	60	2.1
	179	15	400	30	2.8
	180	15	400	45	5.6
	181	15	400	60	7.4
	182	15	420	15	5.9
	183	15	420	30	10.4
	184	15	420	45	12.5
	185	15	420	60	14.8
	186	15	440	15	9.5
	187	15	440	30	14.8
	188	15	440	45	23.1
	189	15	440	60	24.7

Table 6 cont.

Table 6 (Continued)

Compounds	Exp. No.	H_2 pressure/MPa	Temp./°C	Time/min.	Coke/wt%
Hard resin	190	15	460	15	14.2
	191	15	460	30	19.9
	192	15	460	45	26.8
	193	15	460	60	27.5
Soft resin	194	15	400	30	no coke
	195	15	400	60	1.8
	196	15	420	30	3.1
	197	15	420	45	4.4
	198	15	420	60	5.8
	199	15	440	15	3.9
	200	15	440	30	7.2
	201	15	440	45	11.7
	202	15	440	60	14.4
	203	15	460	15	7.4
	204	15	460	30	12.3
	205	15	460	45	15.0
	206	15	460	60	16.4
	207	15	480	15	11.4
	208	15	480	30	17.7
	209	15	480	45	19.9
Aromatics	210	15	440	60	0.7
	211	15	460	30	no coke
	212	15	460	60	1.9
	213	15	480	30	2.2
	214	15	480	45	3.8
	215	15	480	60	5.5
Bitumen	216	15	400	30	2.5
	217	15	400	45	4.5
	218	15	400	60	6.1
	219	15	420	60	9.7
	220	15	440	30	5.9
	221	15	440	45	10.8
	222	15	440	60	12.9

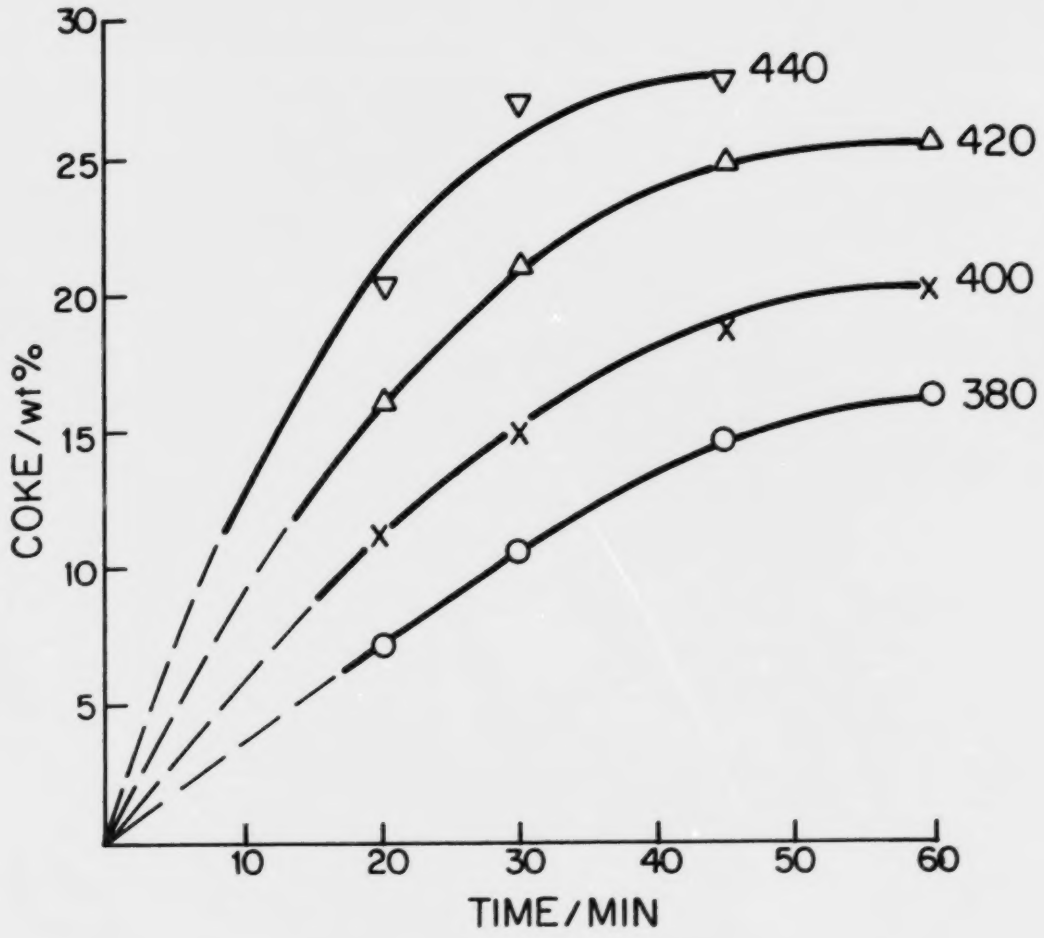


Figure 14: Coke formation as a function of time for Cold Lake asphaltene. Hydrogen pressure = 15 MPa; temperatures as indicated.

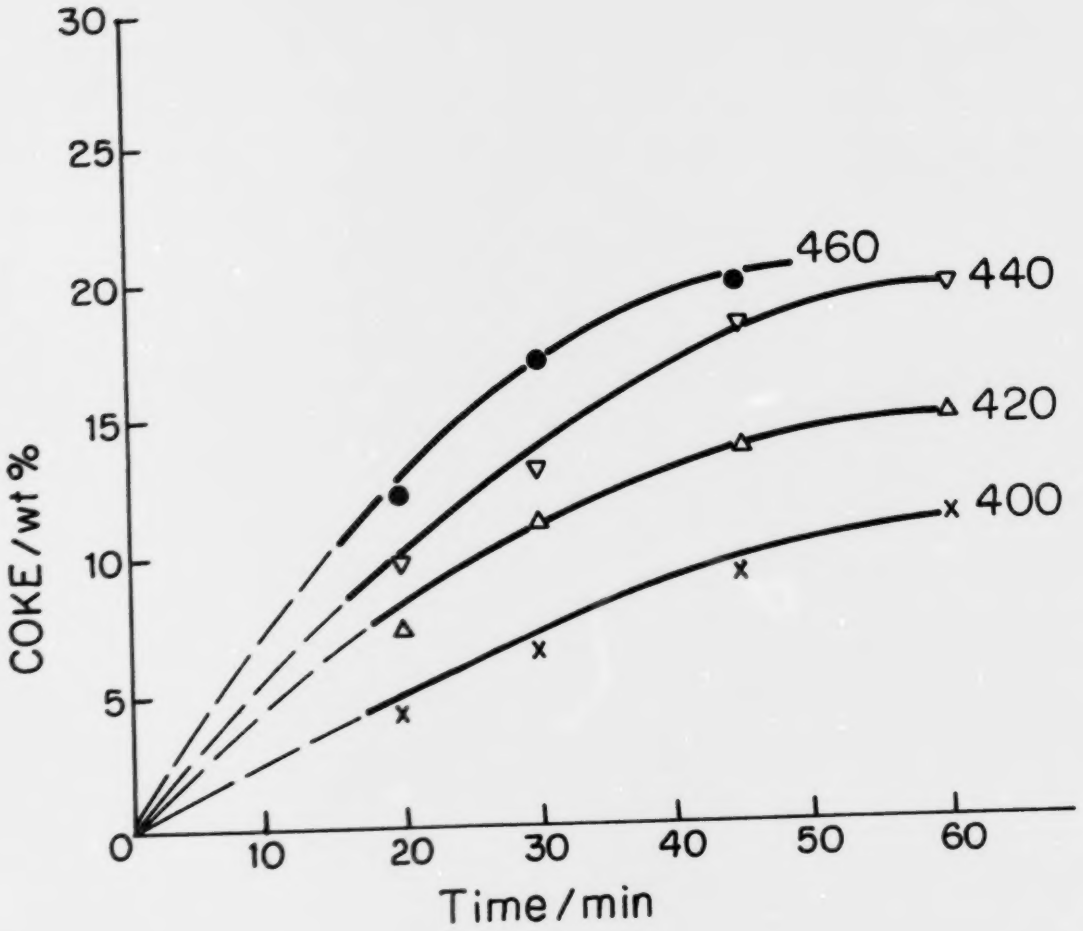


Figure 15: Coke formation as a function of time for Cold Lake hard resin, Hydrogen pressure = 15 MPa; temperatures as indicated.

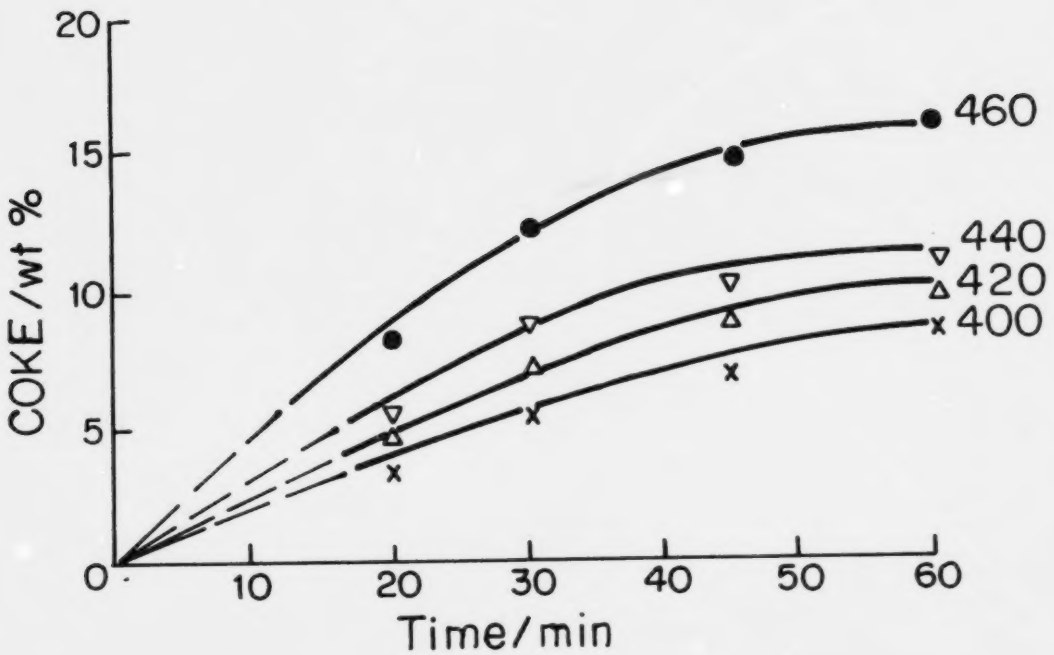
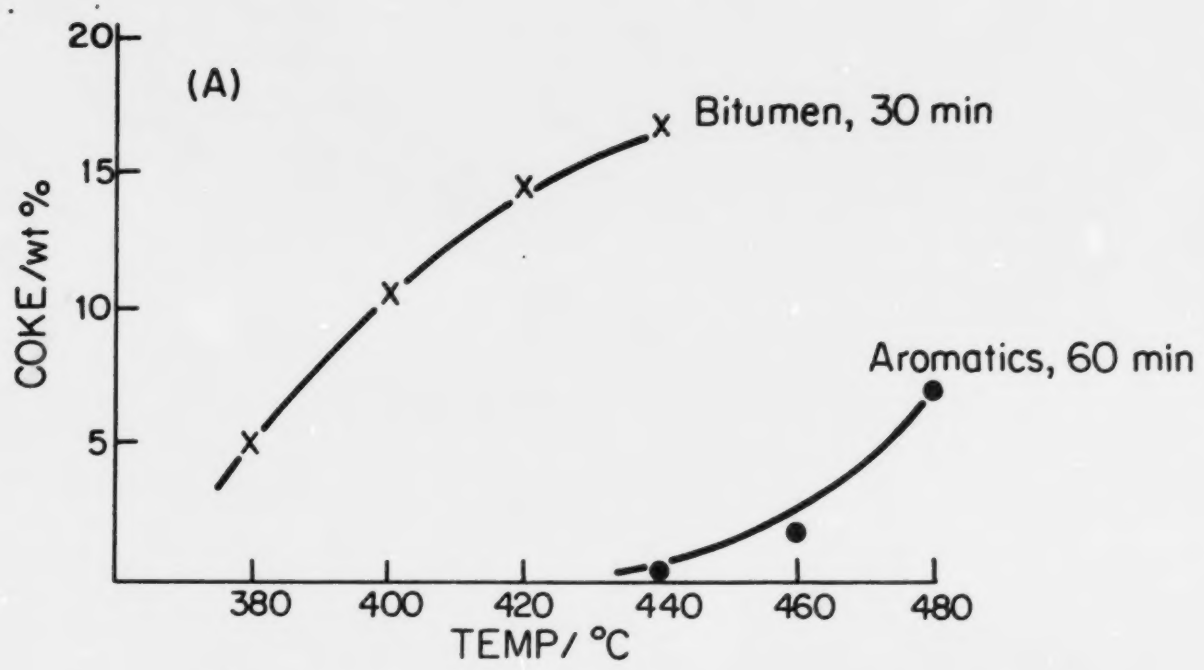


Figure 16: Coke formation as a function of time for Cold Lake soft resin, Hydrogen pressure = 15 MPa; temperatures as indicated.



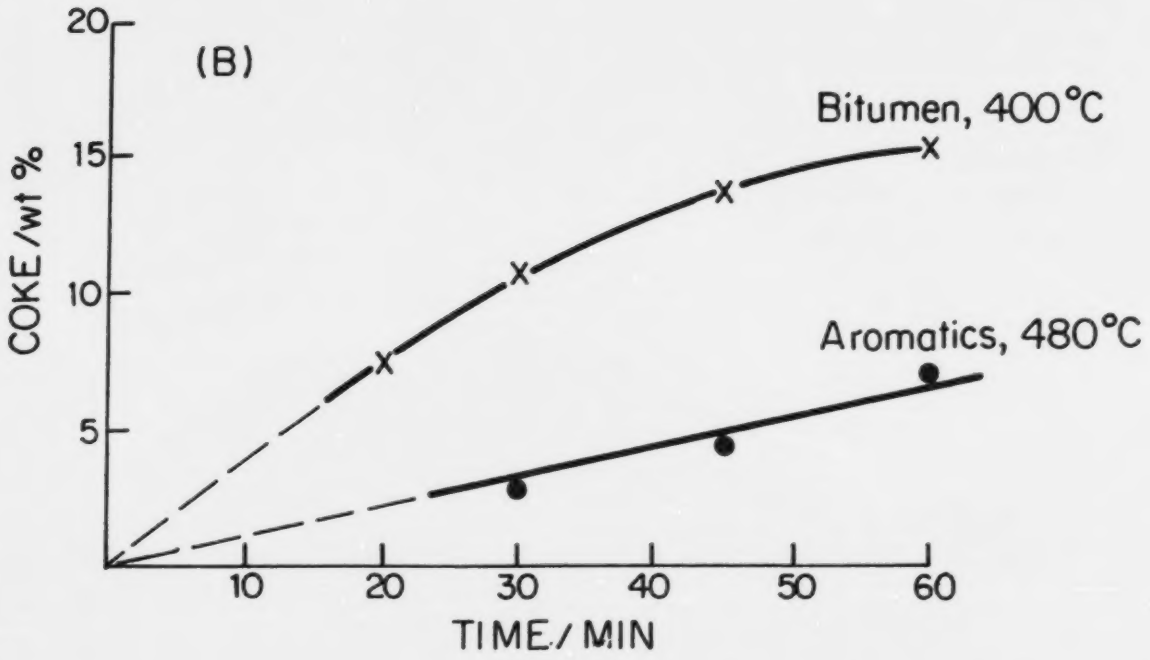


Figure 17: Coke formation from Cold Lake bitumen (X) and Cold Lake aromatics (●). Hydrogen pressure = 15 MPa.

a. Coke produced as a function of temperature, for bitumen after 30 min and for aromatics after 60 min.

b. Coke formation as a function of time, for bitumen at 400°C and for aromatics at 480°C.

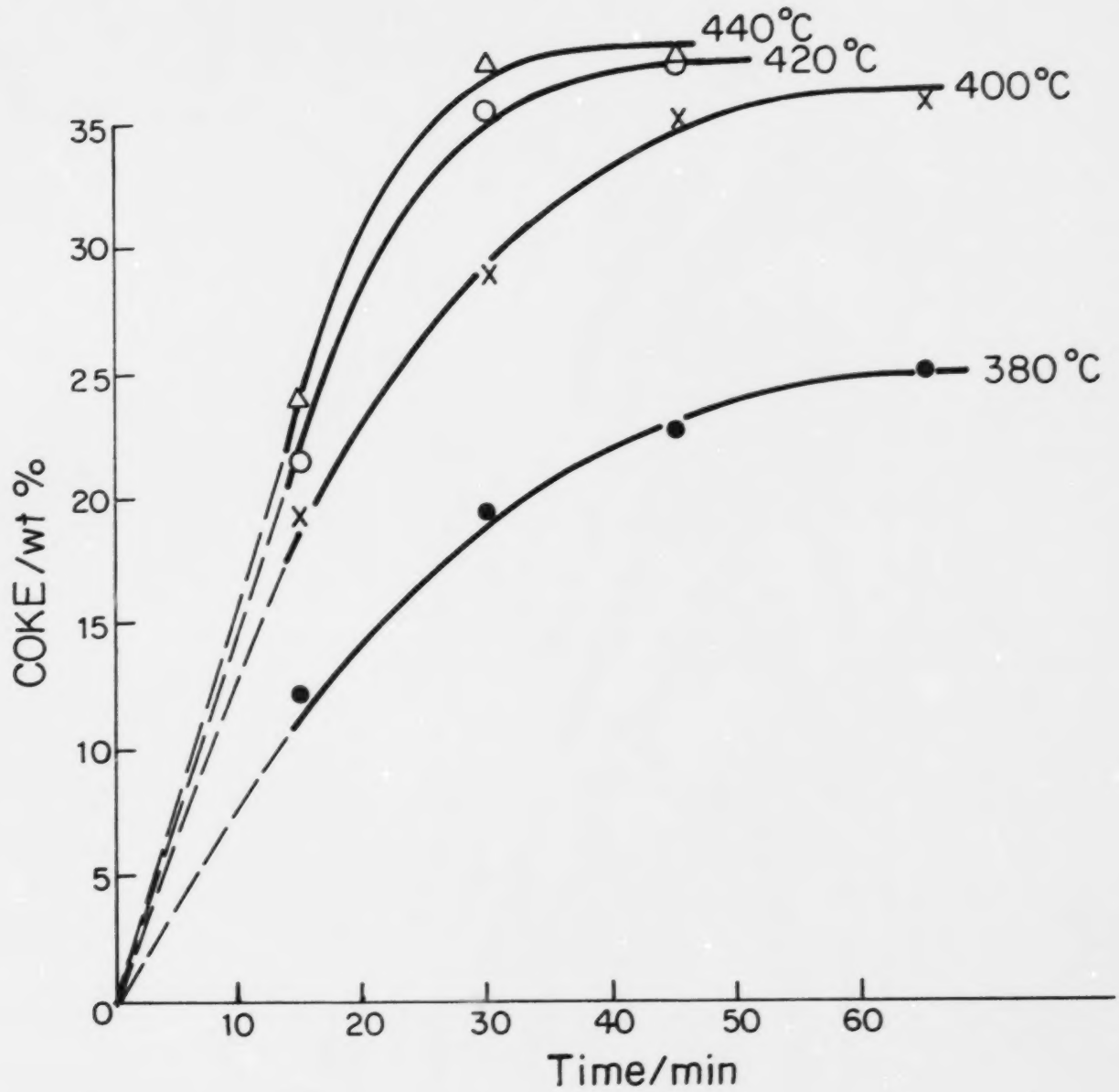


Figure 18: Coke formation as a function of time for Arabian asphaltene.

Hydrogen pressure = 15 MPa; temperatures as indicated.

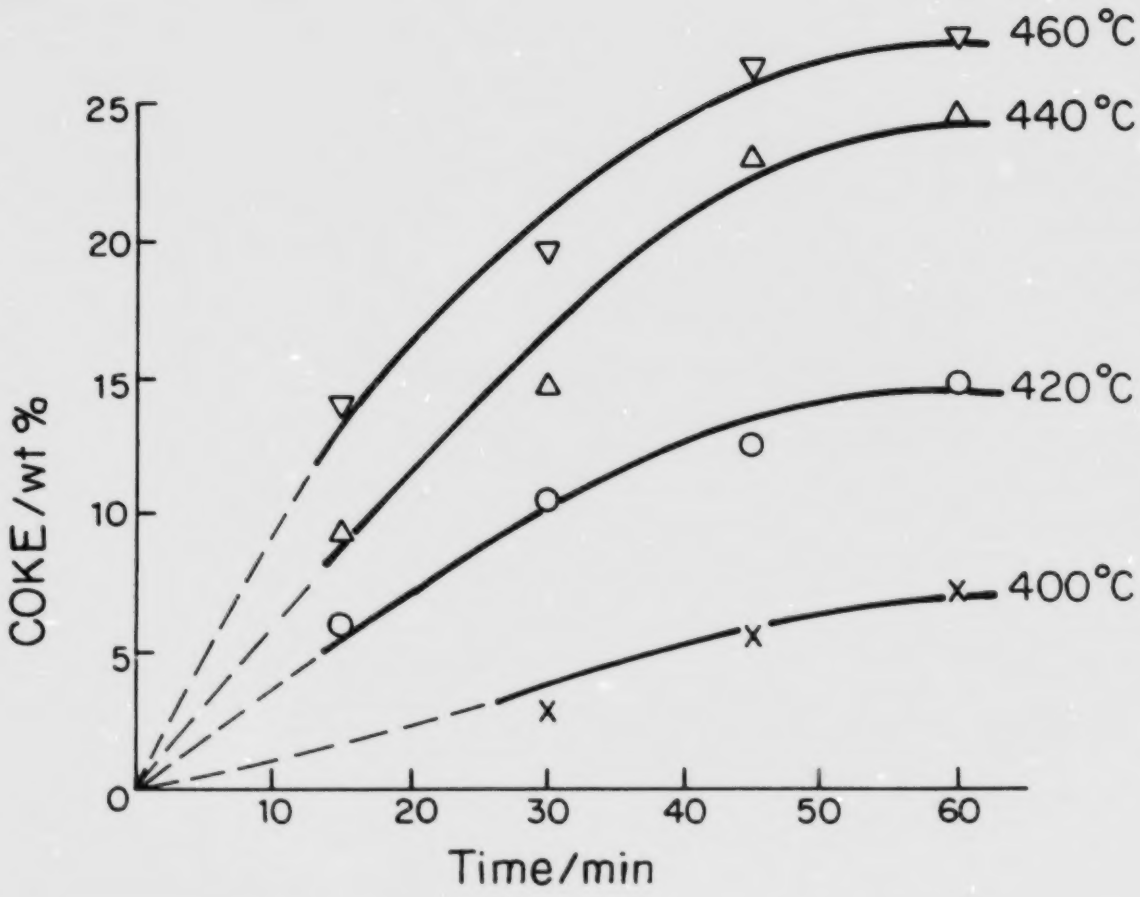


Figure 19: Coke formation as a function of time for Arabian hard resin. Hydrogen pressure = 15 MPa; temperatures as indicated.

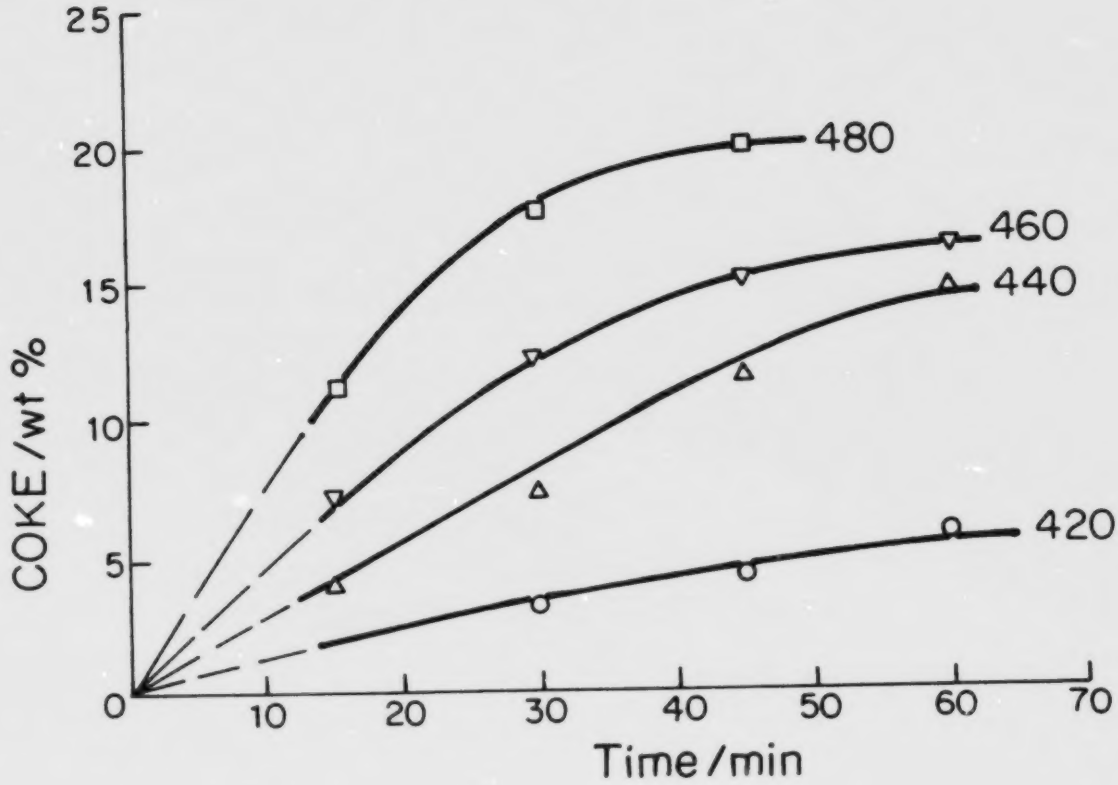


Figure 20: Coke formation as a function of time for Arabian soft resin.

Hydrogen pressure = 15 MPa; temperatures as indicated.

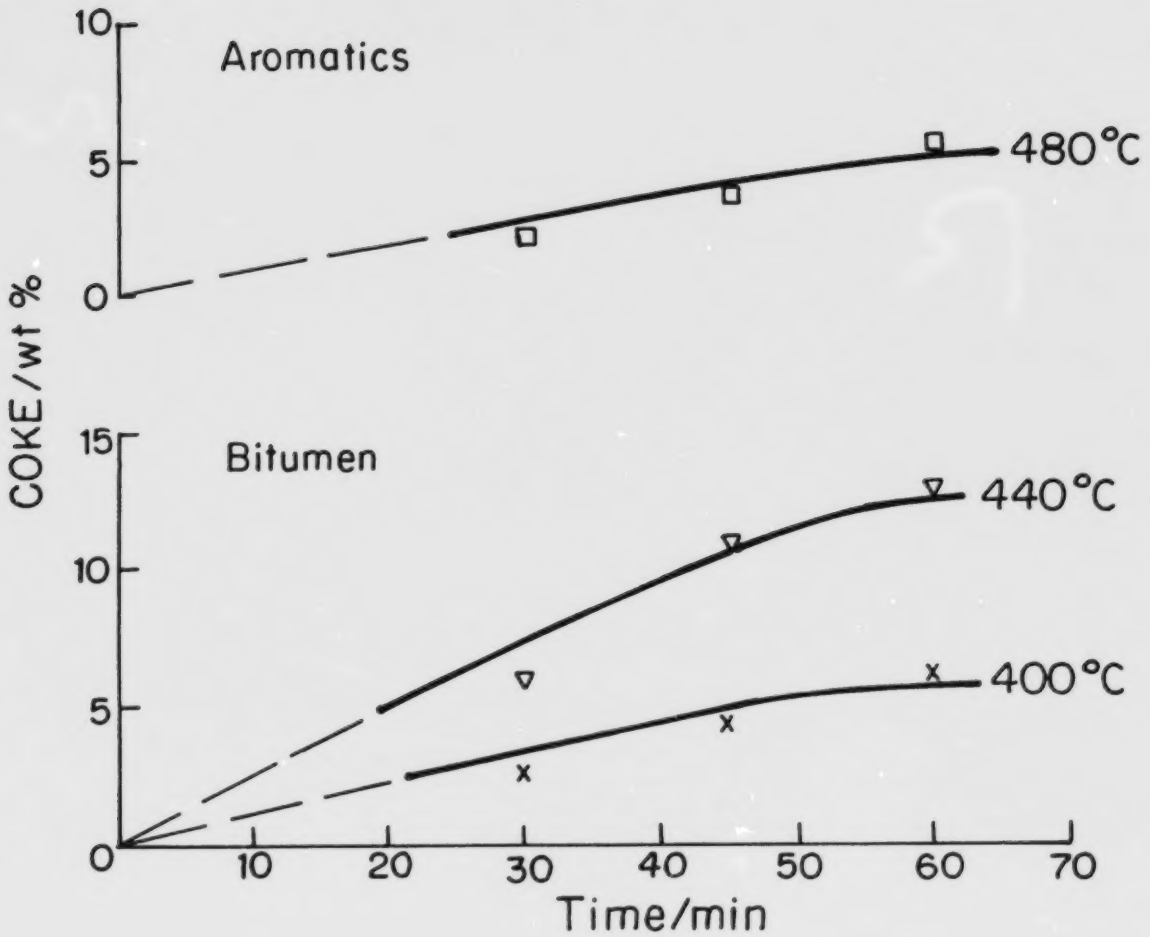


Figure 21: Coke formation as a function of time for Arabian bitumen and aromatics. Hydrogen pressure = 15 MPa; temperatures as indicated.

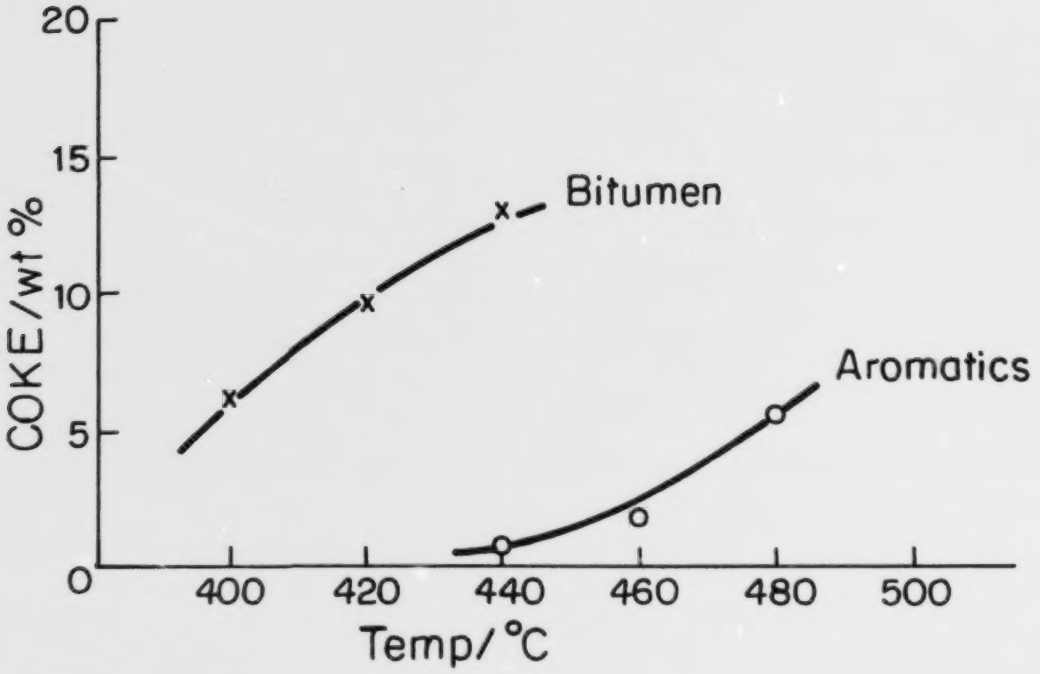


Figure 22: Coke formation as a function of temperature for Arabian bitumen and aromatics. Hydrogen pressure = 15 MPa; reaction time = 60 min.

Discussion

In all cases asphaltene produced much more coke than the resins. At 300°C both resins from Cold Lake bitumen produced about 3% (by weight) of coke in 30 minutes, while resins from Arabian bitumen produced no observable coke under the same conditions. At the same temperature and reaction time Arabian asphaltene produces much more coke (20%) than Cold Lake asphaltene (10%).

Significant results are obtained by comparing the resins from the two sources. As compared to Cold Lake hard resin, Arabian hard resin produced less coke below 420°C, an almost equal amount at 420°C, and more above 420°C. Similarly Arabian soft resin produced less coke below 440°C and more above 440°C, as compared to Cold Lake soft resin.

With the asphaltenes, the Arabian fraction produced more coke than the Cold Lake fraction in all cases, in agreement with our previous suggestion (9) that the amount of coke depends on the aromaticity; Arabian asphaltene is more aromatic than Cold Lake asphaltene. The same is true for the resins above 440°C; however at lower temperatures the situation is reversed, which calls for further investigation.

The aromatic fractions did not produce any coke even at 460°C after 30 min. (Tables 5 and 6); appreciable amounts of coke were obtained only above 480°C. Aromatics from both sources showed the same behaviour; this is consistent with our suggestion (9) since the aromaticity values are the same (H/C = 1.5).

As far as the bitumens themselves are concerned, comparison of Figures 17, 21 and 22 shows that in all cases Cold Lake bitumen produced much more coke than Arabian bitumen. The amount of coke at 400°C from Cold Lake bitumen was more than that obtained from Arabian bitumen at 440°C. It is

concluded, as in the previous work (9), that asphaltene is mainly responsible for coke formation, followed by the resins. Cold Lake bitumen has much more asphaltene (24.5%) than Arabian bitumen (16%), the total resin content being almost the same (Table 2). It therefore seems clear that the large amount of asphaltene in Cold Lake bitumen is responsible for the fact that more coke is formed than from Arabian bitumen.

First-order rate constants for the coke formation from various fractions are presented in Table 7 for the Cold Lake fractions and in Table 8 for the Arabian fractions. It is to be noted that the value for Arabian asphaltene is almost double that for the corresponding resins. In the case of the Cold Lake fractions, the rate constant for asphaltene is about one and a half that of the resins. In both cases the hard and soft resins have quite similar rate constants.

Arabian asphaltene has higher rate constants than Cold Lake asphaltene, and this is in line with the aromaticities. On the other hand, the Arabian resins have lower rate constants than the corresponding Cold Lake fractions. This difference between the behaviour of asphaltene and the resins must be due to some unknown structural differences; this again calls for further study.

Temperature Dependence of Coke Formation

The kinetic measurements were carried out over a range of temperature, and the results are shown in Tables 7 and 8, which includes rate constants (unit: min^{-1}) for four temperatures for each fraction.

Table 7

First-order rate constants for coke formation from Cold Lake fractions (min^{-1})

Temp/^{o}C	Asphaltene	Soft resin	Hard resin
380	0.025	-	-
400	0.031	0.019	0.020
420	0.036	0.023	0.025
440	0.045	0.028	0.029
460	-	0.033	0.035

Table 8

First-order rate constants for coke formation from Arabian fractions (min^{-1})

Temp./^{o}C	Asphaltene	Soft resin	Hard resin
380	0.032	-	-
400	0.037	-	0.019
420	0.040	0.018	0.024
440	0.041	0.020	0.026
460	-	0.025	0.034
480	-	0.033	-

It has been found empirically for a large number of simple and complex chemical processes that rate constants usually vary with temperature according to the Arrhenius equation:

$$k = Ae^{-E/RT}$$

when R is the gas constant (8.314 J K^{-1} mol^{-1}), T the absolute temperature, and A and E are constants. The constant E is the activation energy and for an elementary reaction is the height of the energy barrier that the system has to cross. Coke formation is very far from being an elementary process and no simple significance may be attached to the activation energy; it should simply be regarded as a parameter from which the temperature dependence of the rates can be deduced.

Figures 23 and 24 show Arrhenius plots, of ln k against 1/T, for the three fractions obtained from the two sources of bitumen. The values of E, obtained from the slopes of the plots, are shown in Table 9.

The Arrhenius plots for the Arabian fractions (Fig. 24) show deviations from the Arrhenius equation, the rate constants not changing much with temperature above 420°C. With the resins however, the results are different, there being sharp increases at the higher temperatures (above 460°C for soft resin and above 480°C for hard resin). Curvature of the kind shown for Arabian asphaltene (Fig. 24) is to be explained in terms of consecutive reactions, whereas that for the resins must be due to the occurrence of simultaneous processes during coke formation.

Asphaltene forms coke at a measurable rate at 380°C, but for the resins the rates even at 400°C were very low. For the aromatics it is necessary to go to 460°C to obtain measurable coke formation, and for this reason it was not possible to obtain activation energies.

Table 9

Energies of Activation for coke formation from different bitumens fractions

	Activation Energy/kJ mol^{-1}	
	Cold Lake	Arabian
Asphaltene	34	24
Soft resin	36	30
Hard resin	38	31

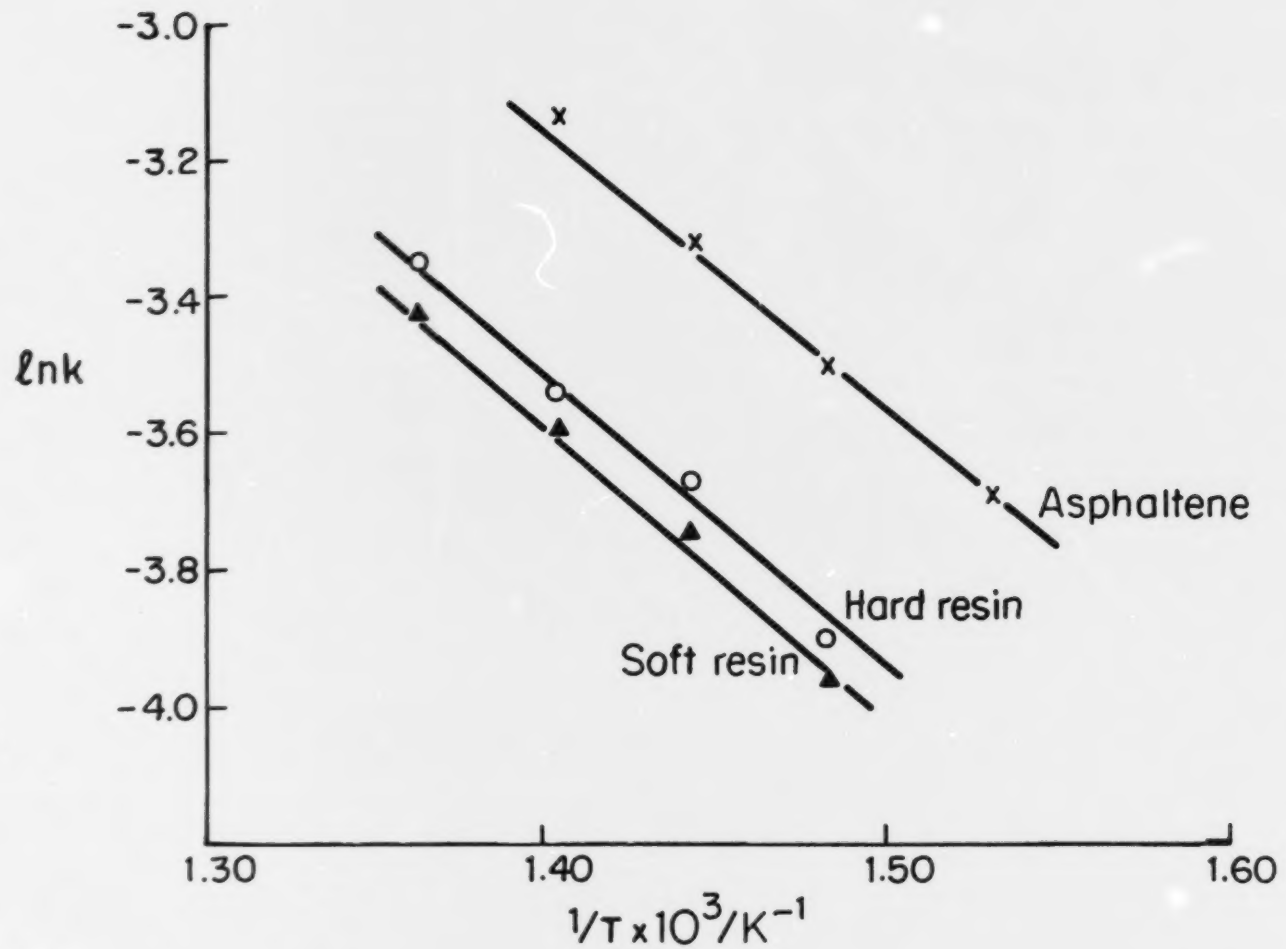


Figure 23: Arrhenius plots for the fractions from Cold Lake bitumen.

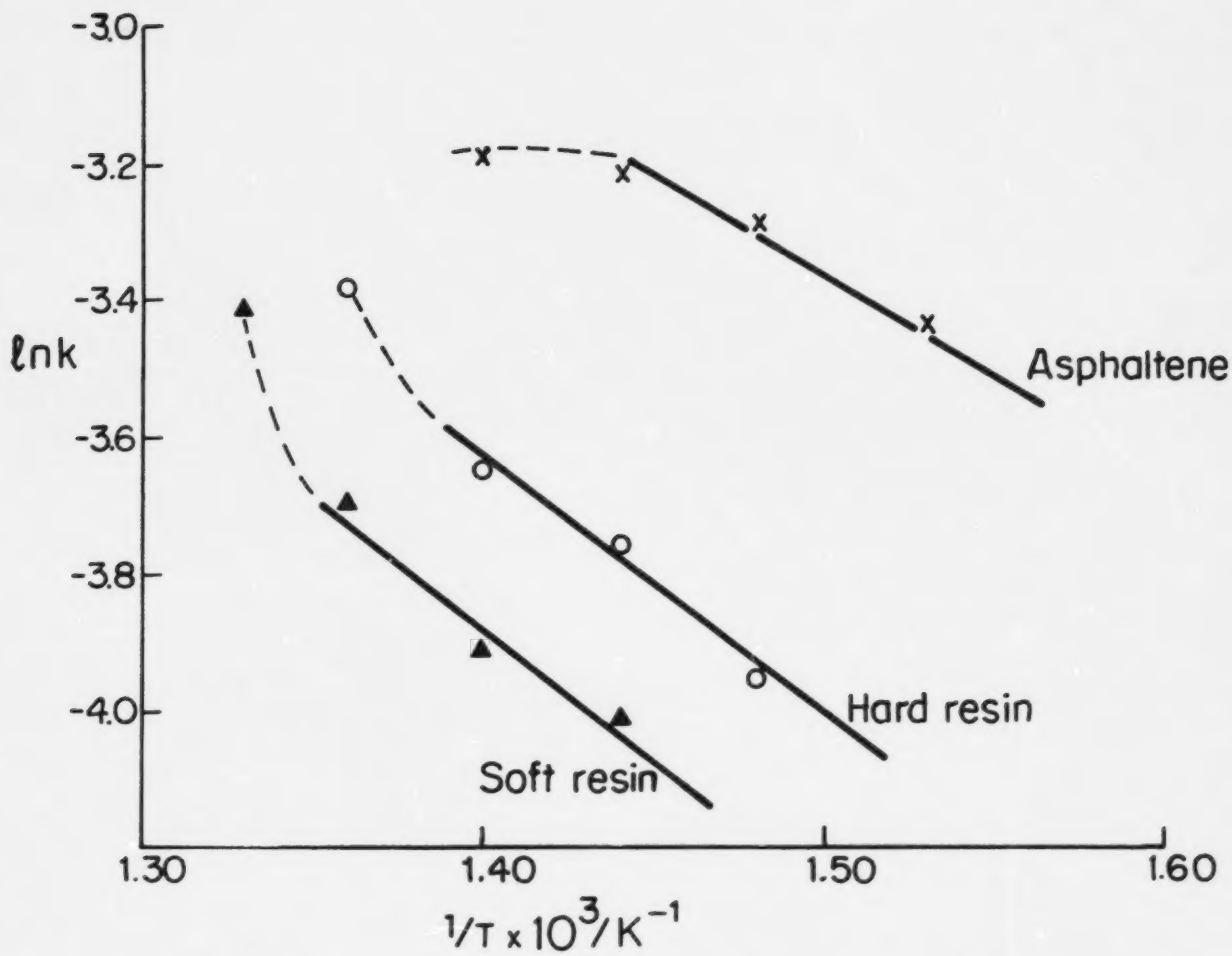


Figure 24: Arrhenius plots for the fractions from Arabian bitumen.

The higher rates of coke formation from the asphaltenes are correlated with the lower activation energies. The differences are particularly striking for the Arabian fractions, the activation energy for asphaltene being 24 kJ mol^{-1}, much lower than the values (30 and 31 kJ mol^{-1}) for the resins.

Comparison of Hydrocracking and Pyrolysis

The present hydrocracking results will now be compared with the results of the pyrolysis experiments described in the previous report (9). Figures 25 and 26 show such a comparison.

In all cases the amounts of coke formed during hydrocracking are considerably smaller than those formed during pyrolysis. In the case of asphaltene, for example, the amounts of coke formed at 400°C after 5 minutes of pyrolysis is about the same as that obtained in 60 minutes of hydrocracking. The rate constant at 400°C for asphaltene is 0.17 min^{-1} for pyrolysis, which is about six times the value (0.03 min^{-1}) for hydrocracking.

Similar differences are found with the resins, again a factor of six being obtained (0.13 min^{-1} for pyrolysis at 400°C, compared with 0.02 min^{-1} for hydrocracking).

In hydrocracking the difference between the hard and soft resins is much greater than in pyrolysis. During hydrocracking hard resin produces much more coke than soft resin, the difference being less in pyrolysis.

In spite of the fact that the rates of coke formation are always lower in hydrocracking than in pyrolysis, the activation energies are significantly lower. This means that the differences are to a great extent due to different pre-exponential factors in the Arrhenius equation.

Figure 25. Results of the pyrolysis (in nitrogen atmosphere) for Cold Lake fractions:

a) Coke formation as a function of time at 400°C, except for aromatics at 470°C.

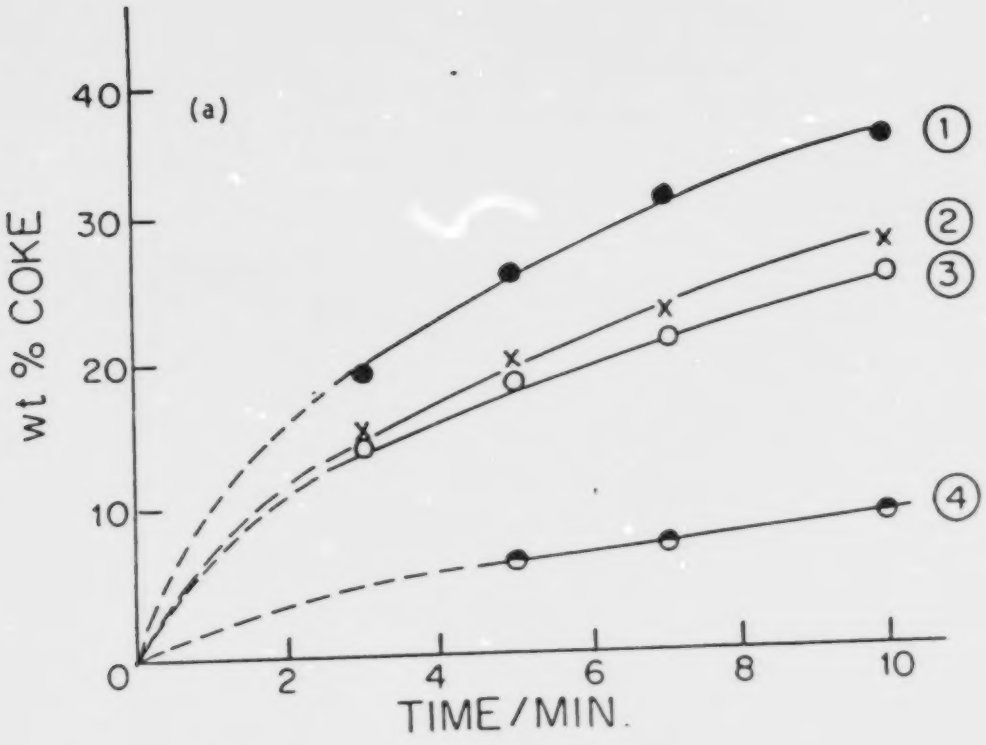
b) Coke formation as a function of temperature at a residence time of 5 minutes.

Figure 26. Results of the hydrocracking of Cold Lake fractions :

a) Coke formation as a function of time at 400°C, except for aromatics at 480°C.

b) Coke formation as a function of temperature at a residence time of 30 minutes, except for aromatics at 60 minutes.

1) Asphaltene
2) Hard resin
3) Soft resin
4) Aromatics
5) Bitumen


(a)
wt % COKE
40
30
20
10
0
2
4
6
8
10
TIME / MIN.
①
②
③
④

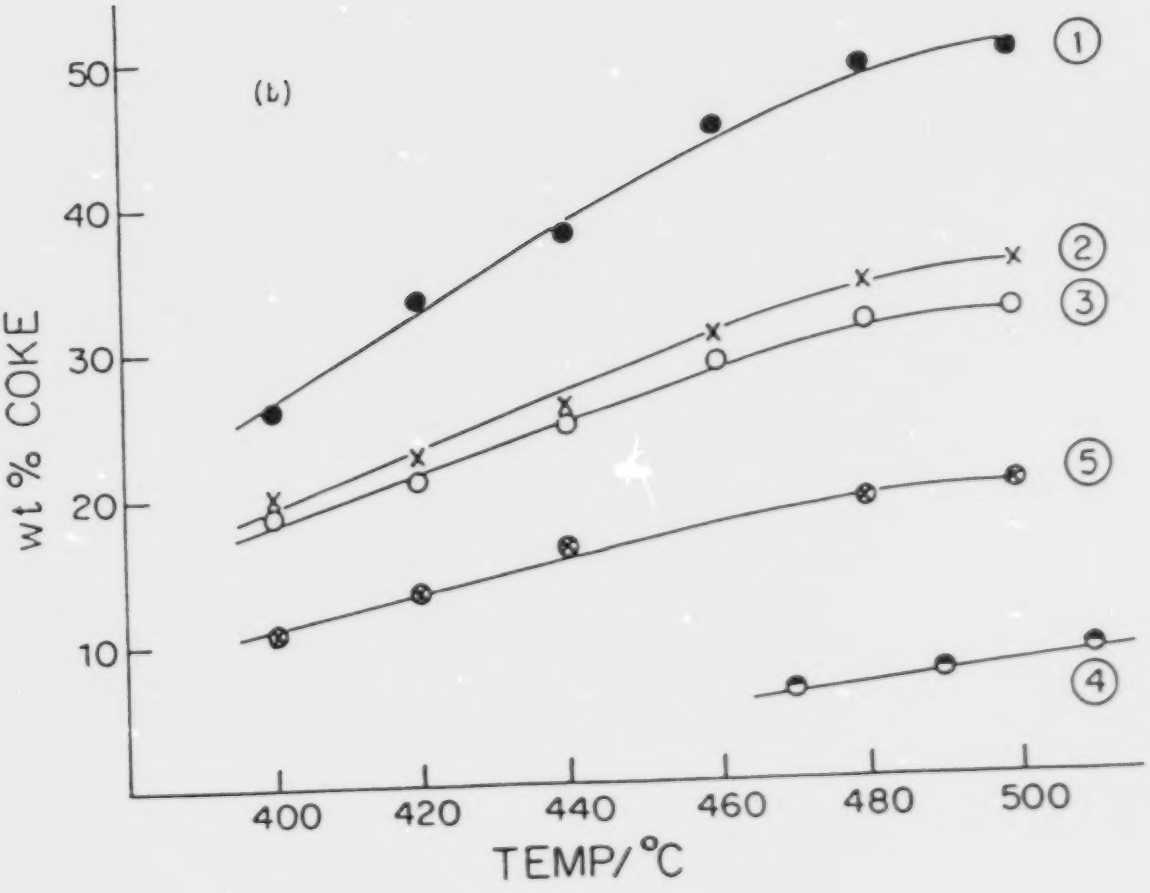

(b)
wt % COKE
50
40
30
20
10
400
420
440
460
480
500
TEMP/ °C
①
②
③
④
⑤

Figure 25

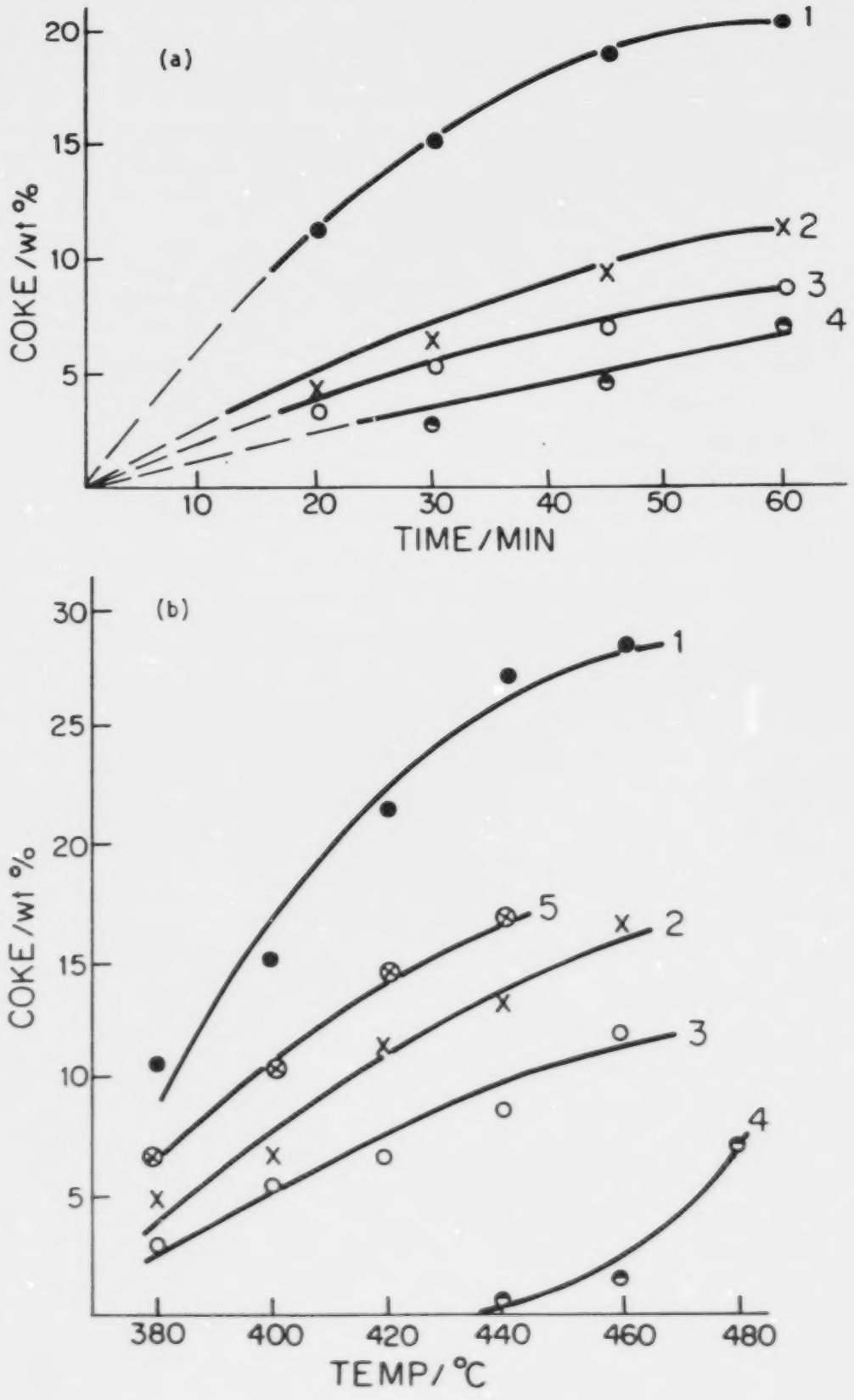
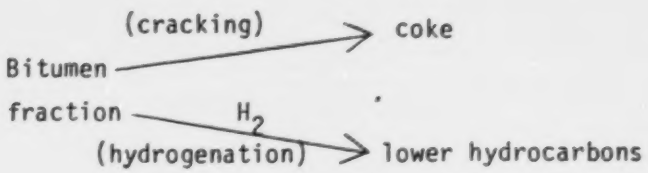


Figure 26

The different rates of coke formation according to whether hydrogen is present or not may be explained on the assumption that coke formation and the hydrogenation processes are in competition with one another:



If the hydrogenation processes have higher activation energies, i.e. higher temperature coefficients, than the cracking processes, there will be relatively more hydrogenation at the higher temperatures; that is, the ratio of hydrogenation to cracking becomes greater as the temperature is raised. The result is that there will be a lower temperature coefficient for coke formation in the presence of hydrogen than in its absence.

PART IV MECHANISMS OF COKE FORMATION

Coke Formation in the Presence of Sulfur

The results presented in Part II showed that the addition of small amounts of sulfur, less than 7%, reduces the coke formation at lower temperatures; in the case of asphaltenes this was true at temperatures below 380°C, while for resins it was true for temperatures below 400°C. At higher temperatures the addition of sulfur brought about an increase in coke formation.

The following type of mechanism provides a possible explanation for these results. A substance Ar-R, present in bitumen and its components, will undergo dissociation to give free radicals

$$Ar - R \longrightarrow Ar\cdot + R\cdot \qquad (1)$$

In the presence of sulfur these radicals will undergo reactions of the following types:

$$2Ar\cdot + S \longrightarrow Ar\text{-}S\text{-}Ar \qquad (2)$$

$$2Ar\cdot + S \longrightarrow R\text{-}S\text{-}R \qquad (3)$$

$$Ar\cdot + R\cdot + S \longrightarrow R\text{-}S\text{-}Ar \qquad (4)$$

$$2Ar\cdot + 2S \longrightarrow Ar\text{-}S\text{-}S\text{-}Ar \qquad (5)$$

and so on. These reactions may predominate at the lower temperatures, and under these conditions the sulfur is removing free radicals and thus inhibiting the polycondensation reactions that are responsible for coke formation.

At higher temperatures there will be a relatively greater rate of formation of radicals, since the activation energy for these processes is greater than that for reactions such as (2)-(5). Also, at higher temperatures the sulfur atoms may abstract hydrogen atoms by reactions such as

$$\text{Ar-H} + \text{S} \longrightarrow \text{Ar}\cdot + \text{HS} \qquad (6)$$

$$\text{HS} + \text{Ar-H} \longrightarrow \text{Ar}\cdot + \text{H}_2\text{S} \qquad (7)$$

Because of reactions of this type, at higher temperatures sulfur aids coke formation, since it brings about the formation of more organic radicals which by addition to one another form coke.

Also, at higher temperatures the sulfur-containing compounds obtained in reactions such as (4) and (5) remain in the coke. They are insoluble in toluene and therefore appear as coke in the present experiments.

Coke Formation During Hydrocracking

The work described in Part III has shown that during hydrocracking the rate of coke formation is considerably less, by a factor of six or so, than the rate during pyrolysis in the absence of hydrogen. The order of the rates coke formation was the same in the two types of process, being

asphaltene > hard resin > soft resin > aromatics

The aromatics produce coke extremely slowly, and the saturates not at all under our experimental conditions. As noted earlier (9) for pyrolysis, and found again in the present hydrocracking work (Part III), the rates are strongly correlated with the aromaticities. Other factors are, however, significant. Thus Arabian resins are more aromatic than Cold Lake resins, but did not always produce more coke. Also, hard resins produce more coke than soft resins, although the aromaticities are almost the same.

A general reaction scheme that is consistent with these results is as follows:

$$\text{Ar-R} \longrightarrow \text{Ar}\cdot + \text{R}\cdot \qquad (1)$$

$$\text{R}\cdot + \text{H}_2 \longrightarrow \text{RH} + \text{H}\cdot \qquad (2)$$

$$\text{Ar}\cdot + \text{H}_2 \longrightarrow \text{ArH} + \text{H}\cdot \qquad (3)$$

$$\text{Ar-R} + \text{R}\cdot \longrightarrow \text{Ar-R}\cdot + \text{RH} \qquad (4)$$

$$\text{Ar-R} + \text{H}\cdot \longrightarrow \text{Ar-R}\cdot + \text{H}_2 \qquad (5)$$

$$2\text{Ar-R}\cdot \longrightarrow \text{Ar-R-R-Ar} \qquad (6)$$

By a continuation of processes of this kind, products of higher and higher molecular weights are formed, and the result is the formation of coke.

Reactions such as (2) and (3) are stabilizing reactions; they remove organic radicals from the system and hence reduce coke formation. This explains why the presence of hydrogen inhibits coke formation, as found in the present work. Hydrogen molecules themselves do not dissociate easily at the temperature used, since the strength of the H-H bond (432 kJ mol^{-1}) is high. The strength of carbon-carbon bonds is considerably lower (~360 kJ mol^{-1}), so that at temperatures used in the present work and in the technical process there can be a significant amount of free-radical formation by reactions of the type of reaction (1).

To explain the relative rates of coke formation from the various bitumen fractions the scheme of reactions shown in Figure 27 is tentatively suggested. The coke is formed from large aromatics, which can be produced relatively rapidly from the asphaltenes. Resins, which form coke less rapidly, do so either by first forming asphaltenes (reaction 6) or directly (reaction 3), but these reactions are slow. The reactions involving the aromatics (reactions 5 and 2) are even slower.

In the presence of hydrogen the substances will become hydrogenated (reactions 7, 8 and 9), with the formation of more saturated compounds which produce coke with greater difficulty. Two competitive sets of reactions therefore occur in the presence of hydrogen. At large enough hydrogen pressures the hydrogenation reactions, leading to the formation of saturated compounds, will be important enough to give a substantial reduction in coke formation.

The curvatures found in the Arrhenius plots (Figures 23 and 24) support this proposed reaction scheme. In the case of the asphaltenes the curvature is concave towards the axes, and this indicates the importance of consecutive reactions; these are reactions 4 and 1. For the resins, on the other hand, the curvature is convex towards the axes, and this is indicative of the importance of parallel reactions. According to the suggested scheme, the resins form coke by way of reactions 3 and 6, which occur in parallel.

Summary of Conclusions

The main conclusions from the previous work (9) and from the work described in the present report may be summarized briefly as follows. Cracking reactions become important at 380°C for the asphaltenes, and for the resins at 400°C. At all temperatures investigated the coke comes primarily from the

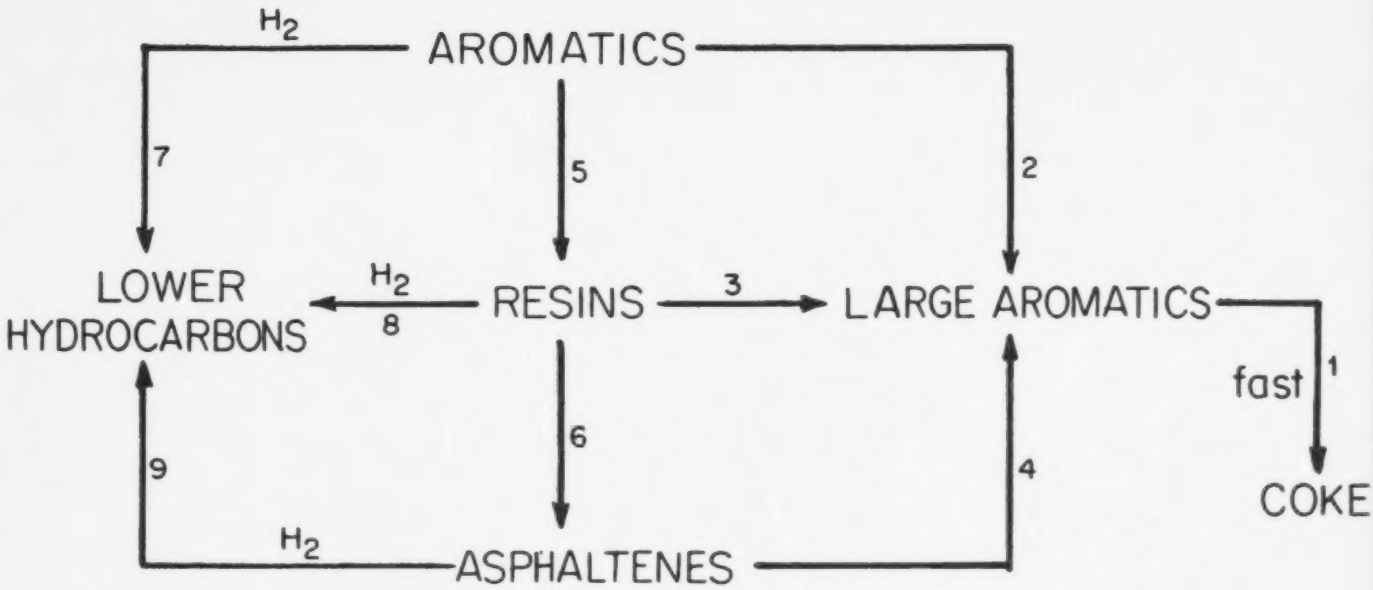


Figure 27 . Tentative reaction scheme of Coke formation from different fractions of bitumen during Hydrocracking process.

asphaltenes, to a smaller extent from the resins, and hardly at all from the aromatics and the saturated compounds.

In the presence of small amounts of sulfur (less than 7%) there is a reduction in coke formation at lower temperatures (below 380°C), while at higher temperatures the addition of sulfur brought about an increase in coke formation. This effect is attributed to reactions between free radicals and sulfur.

In the presence of hydrogen the rate of coke formation was considerably lower than in its absence, but the order with which coke was formed from the different fractions is the same in the two cases. This effect is attributed to a competition between the cracking and hydrogenation processes.

APPENDIX

For convenience some additional information is included in this appendix.

Calculation of Rate Constants

The rate constants for coke formation were calculated from the initial rates using the differential method introduced by J.H. van't Hoff (Etudes de dynamique chimique, Amsterdam, 1884). For a first-order reaction

$$\frac{dx}{dt} = kx_o,$$

where x is the amount of coke formed at any time and x_o the amount after infinite time. The slopes dx/dt were measured at the beginning of the reaction (t = 0), and division by x_o gives the rate constant.

For reactions of any complexity, such as the one being studied, this procedure is the most reliable, since it avoids complications such as the influence of reaction products on the rate. Studies of the time-course of the reactions, by analyzing the form of the curves showing x as a function of time, could be the subject of further investigation, and would provide information as to product effects. It was considered more useful to concentrate on initial coking rates in the present study.

Coke Formed From Components, As Compared With That Formed From Bituman

Table A1 shows a comparison of the amounts of coke formed from the bitumen with the sum of the amounts formed from the components. In all cases, the total amounts obtained from the components were less than the amounts obtained from the bitumen itself, except for Arabian at 400°C.

Additional NMR and IR Records

Figures A1 to A8 show additional NMR records, and Figures A9 to A12 show additional infrared records.

Table A1

Coke Formation from Bitumens and their Fractions.

	Temp./°C	Time/min.	Coke from bitumen wt. %	Σ Coke from fractions wt.%
Arabian	400	30	2.5	4.6
	440	45	10.8	9.7
Cold Lake	400	30	10.4	5.1
	440	30	16.7	9.2

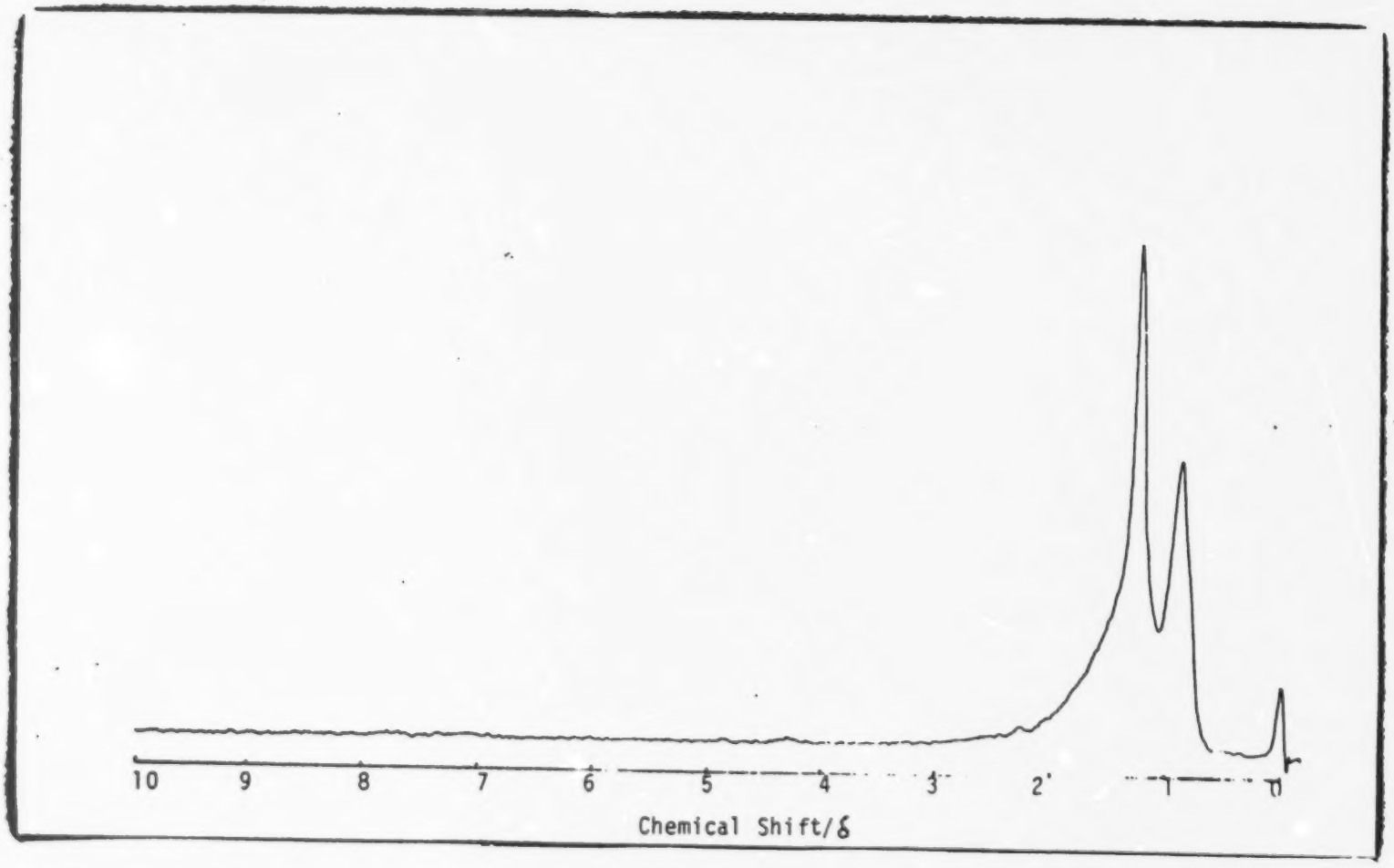


Figure A1. Nuclear magnetic resonance spectroscopy records for saturates from Cold Lake bitumen

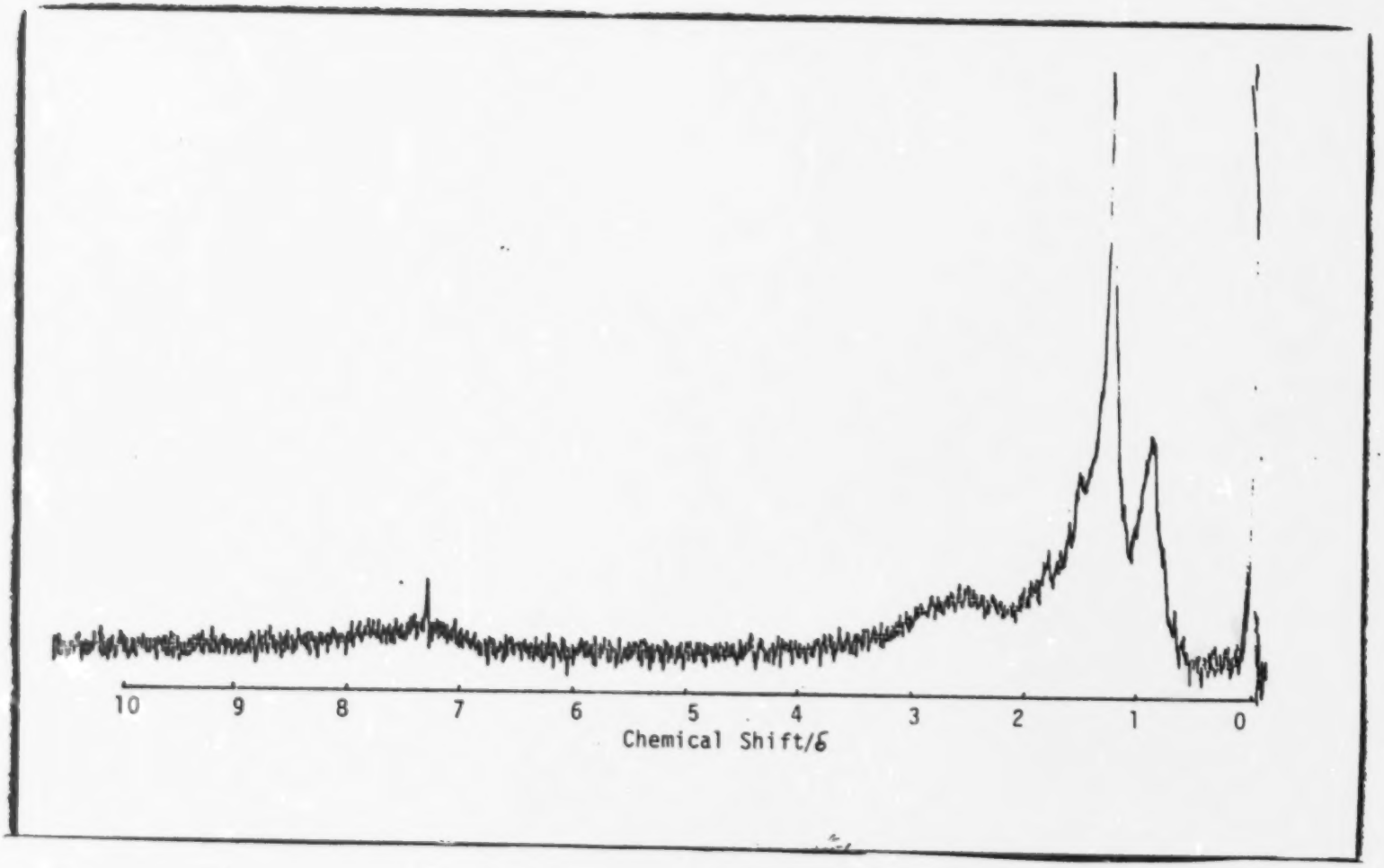


Figure A2. Nuclear magnetic resonance spectroscopy records for aromatics from Cold Lake bitumen

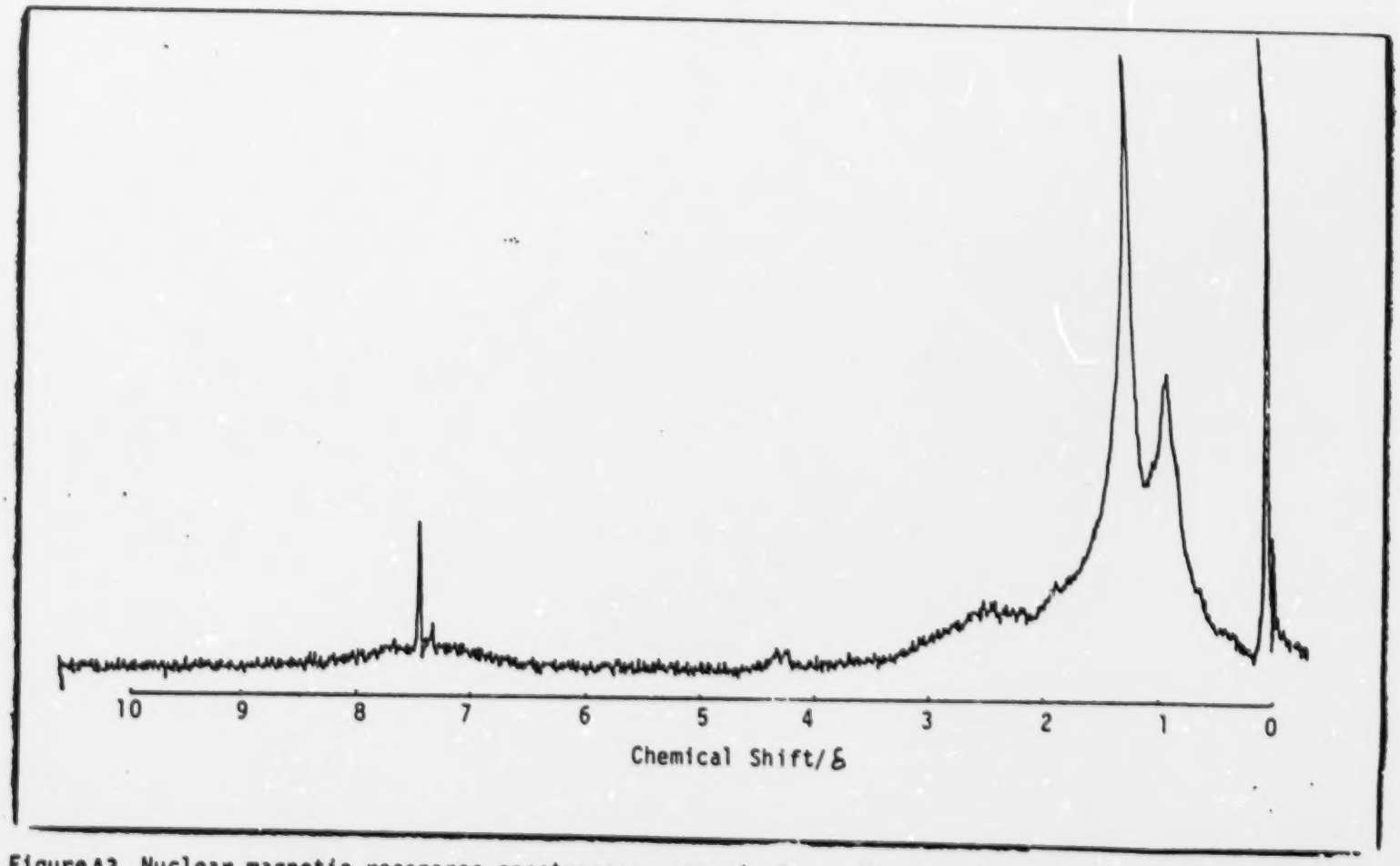


Figure A3. Nuclear magnetic resonance spectroscopy records for soft resin from Cold Lake bitumen

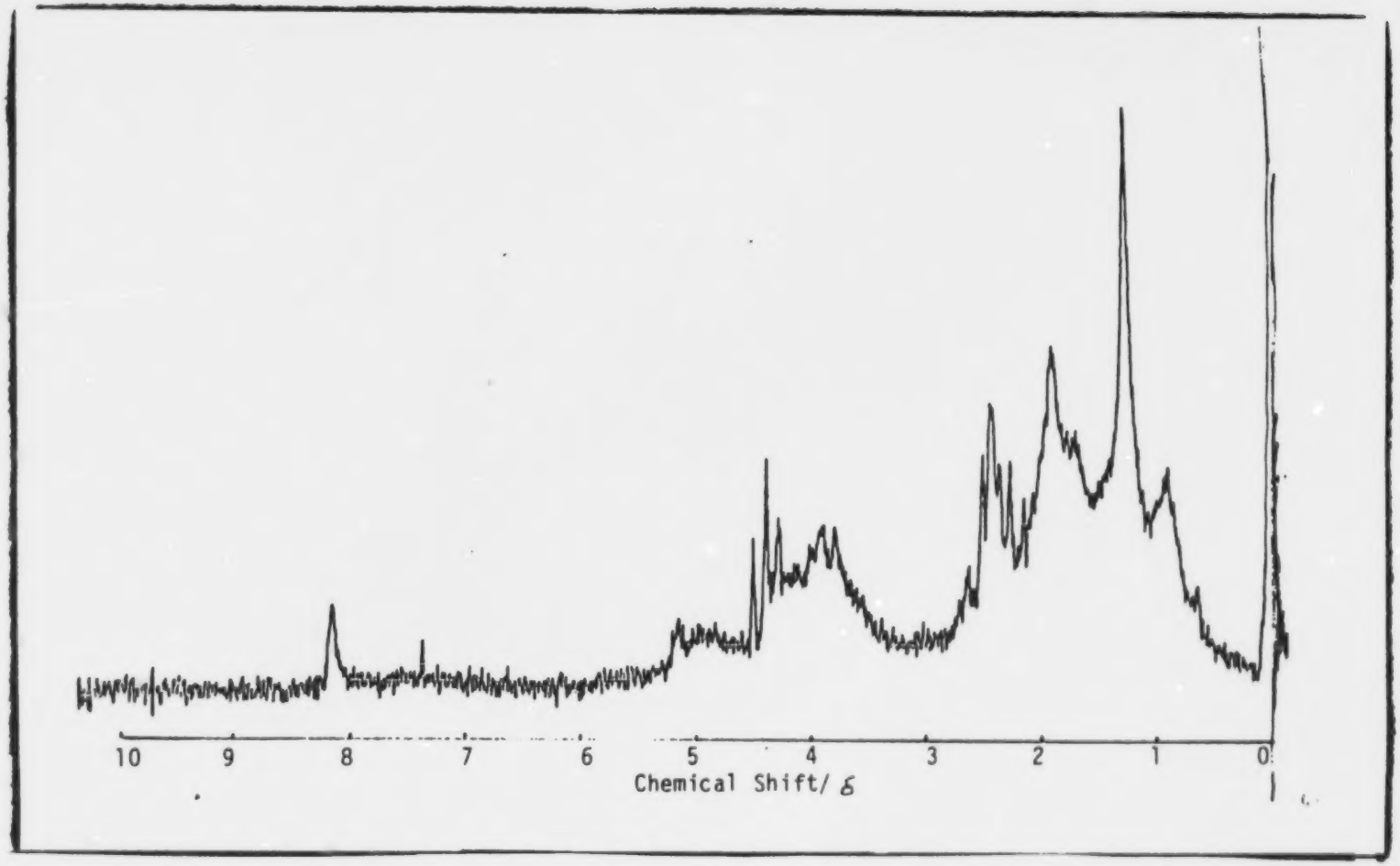


Figure A4. Nuclear magnetic resonance spectroscopy records for hard resin from Cold Lake bitumen

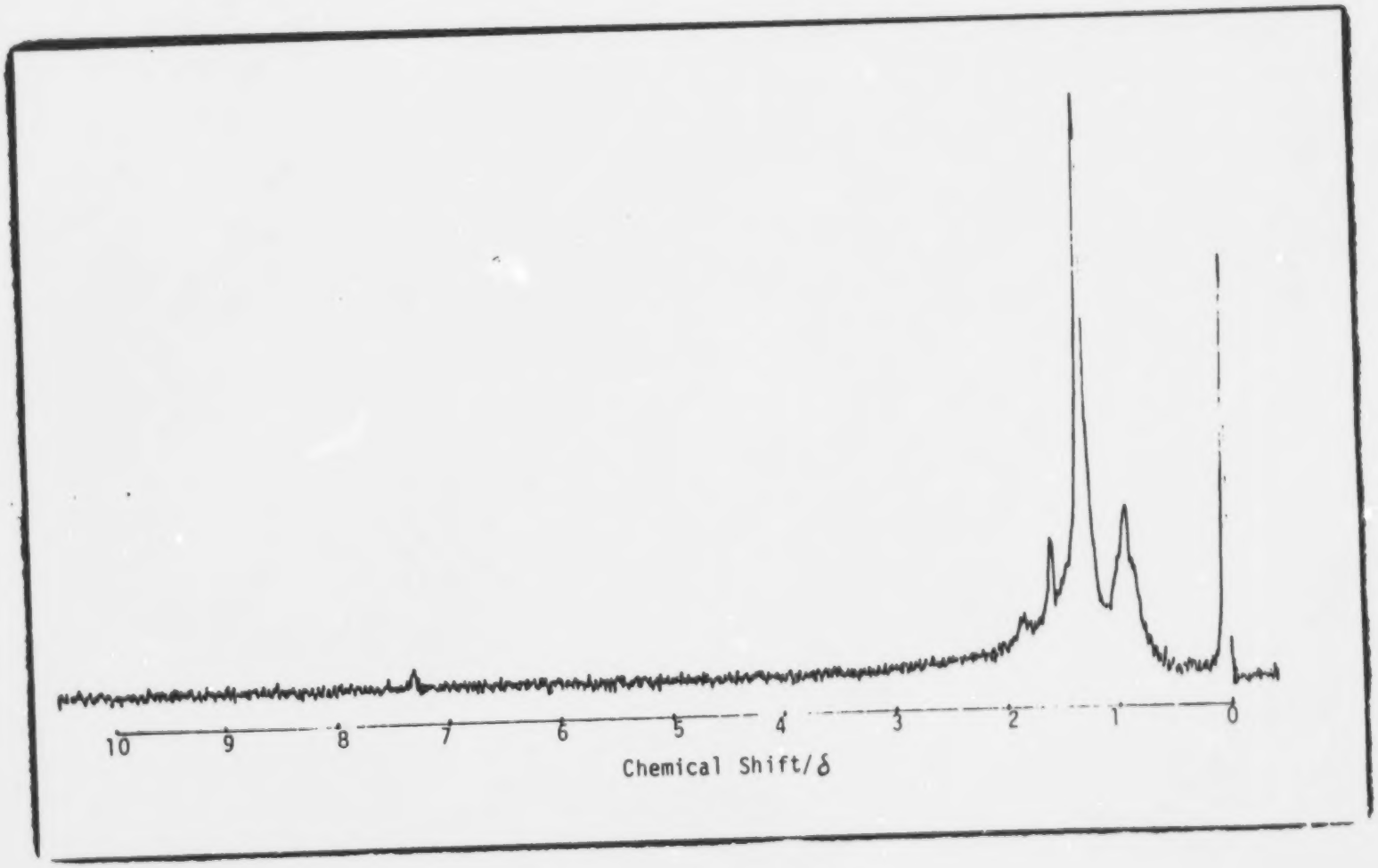


Figure A5. Nuclear magnetic resonance spectroscopy records for saturates from Arabian bitumen

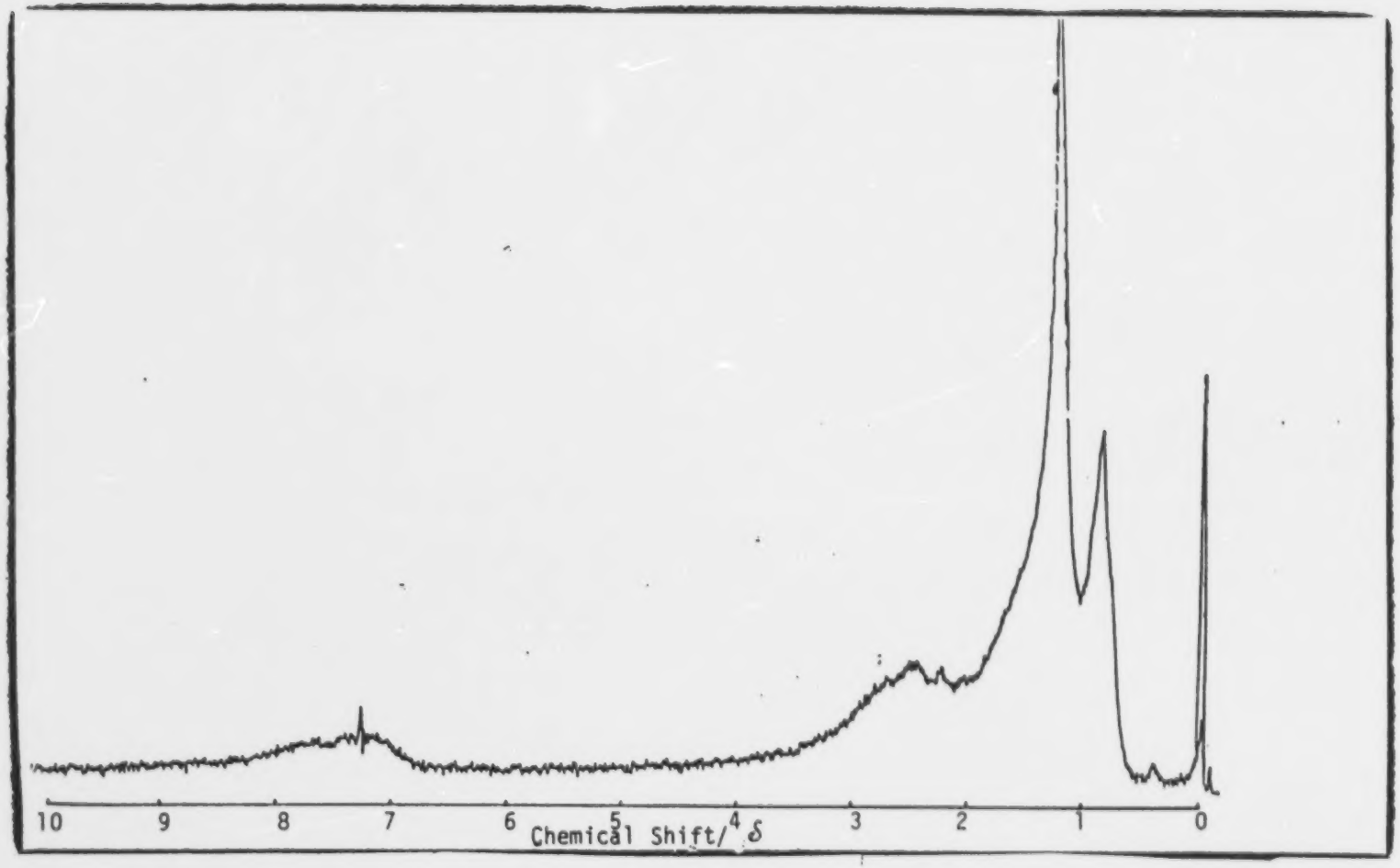


Figure A6 . . Nuclear magnetic resonance spectroscopy records for aromatics Arabian bitumen

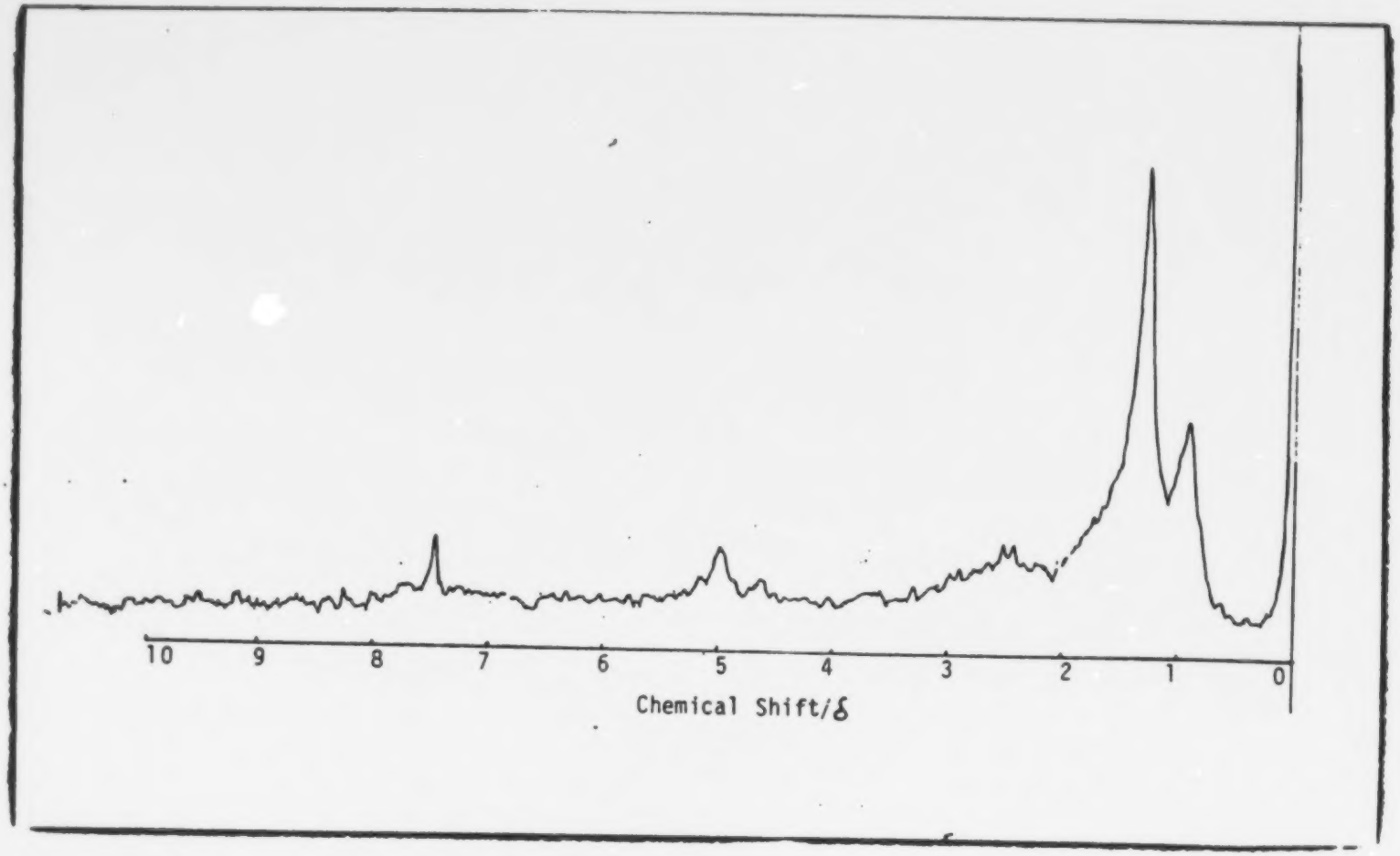


Figure A7. Nuclear magnetic resonance spectroscopy records for soft resin from Arabian bitumen

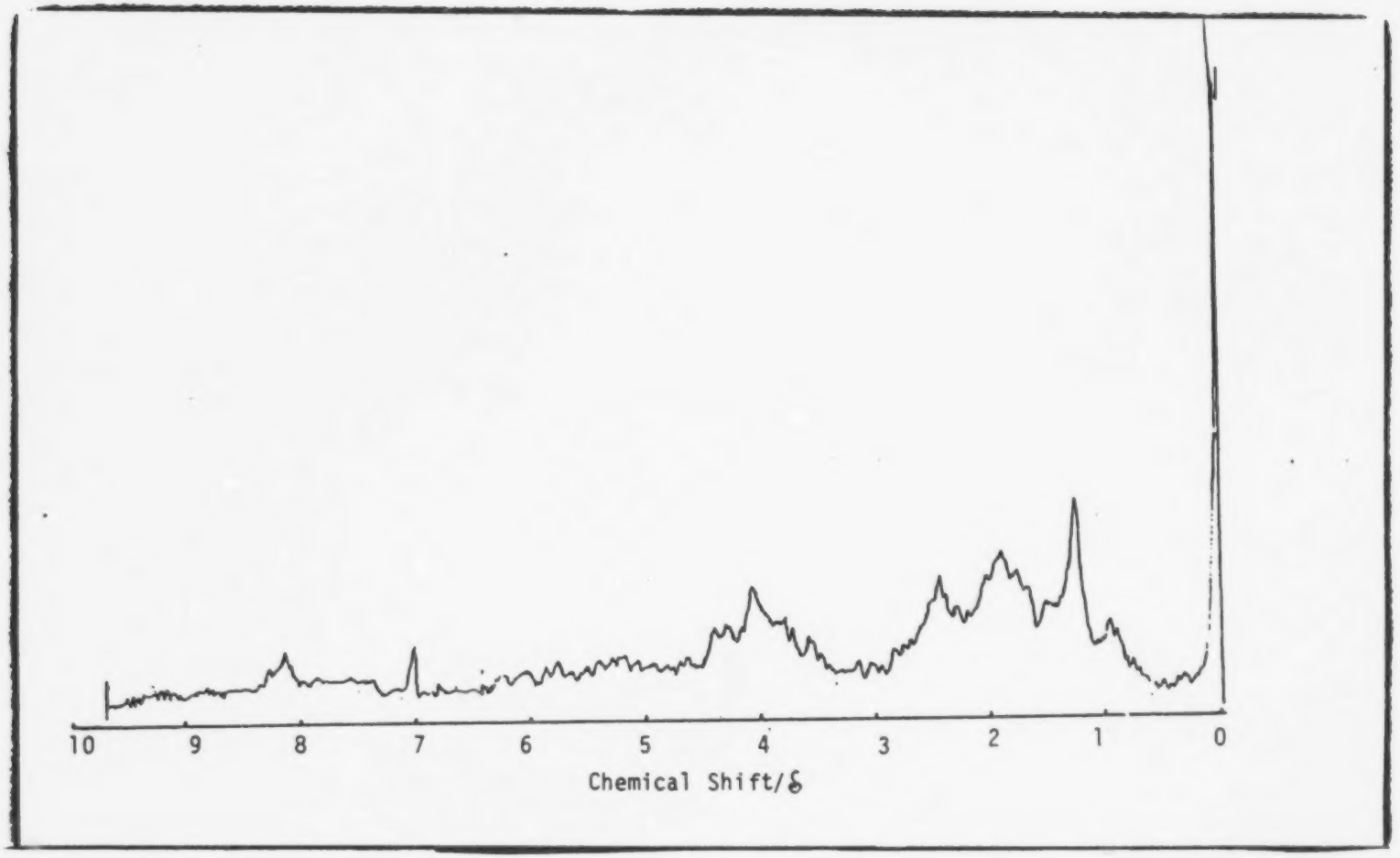


Figure A8. Nuclear magnetic resonance spectroscopy records for hard resin from Arabian bitumen

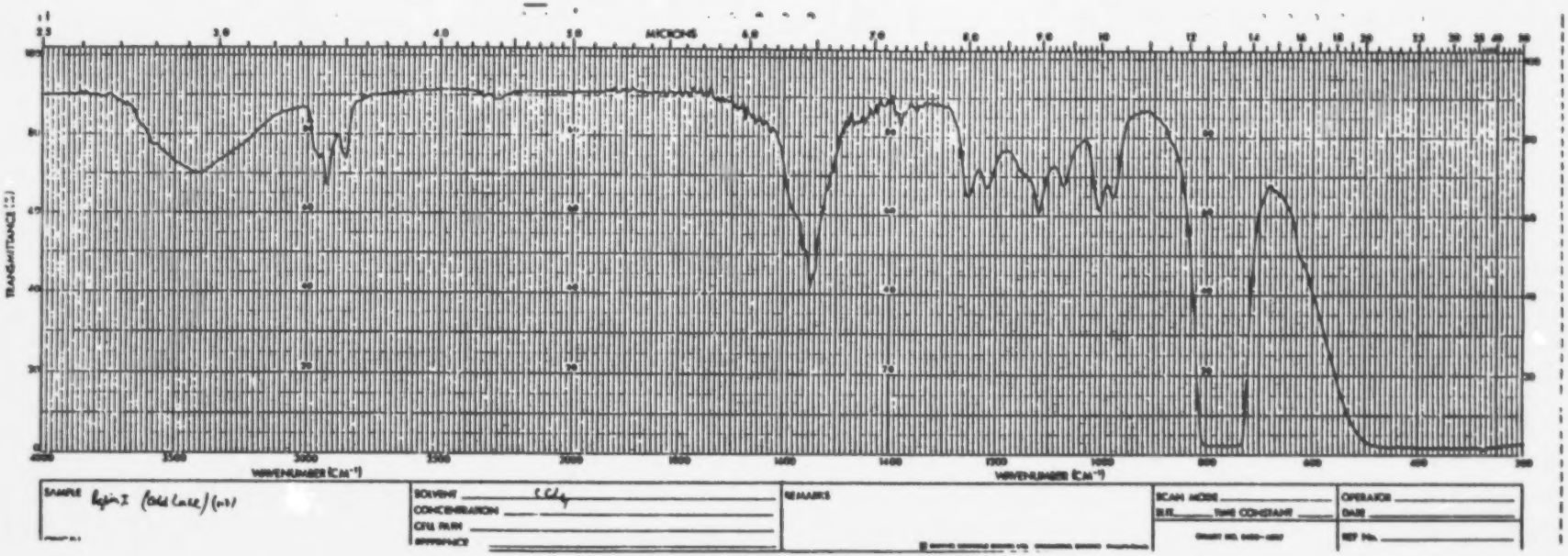


Figure A9. Infrared record for soft resin from Cold Lake bitumen in CCl_4.

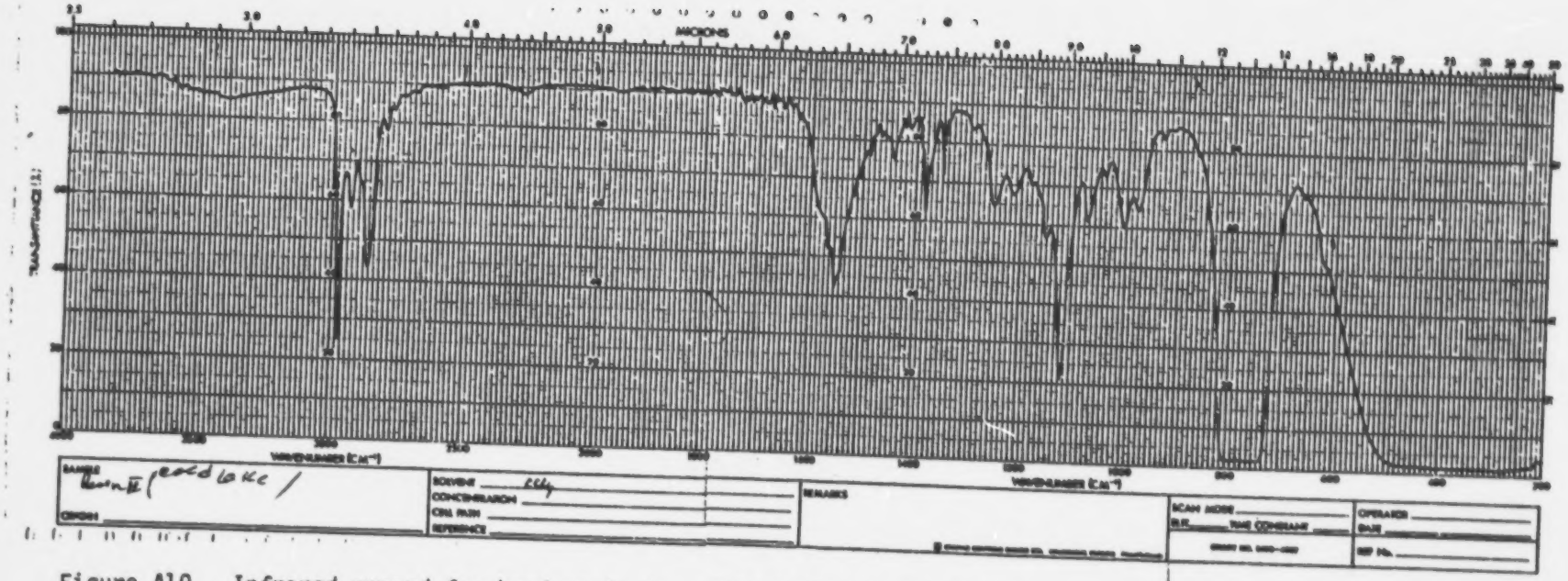


Figure A10 . Infrared record for hard resin from Cold Lake bitumen in CCl_4

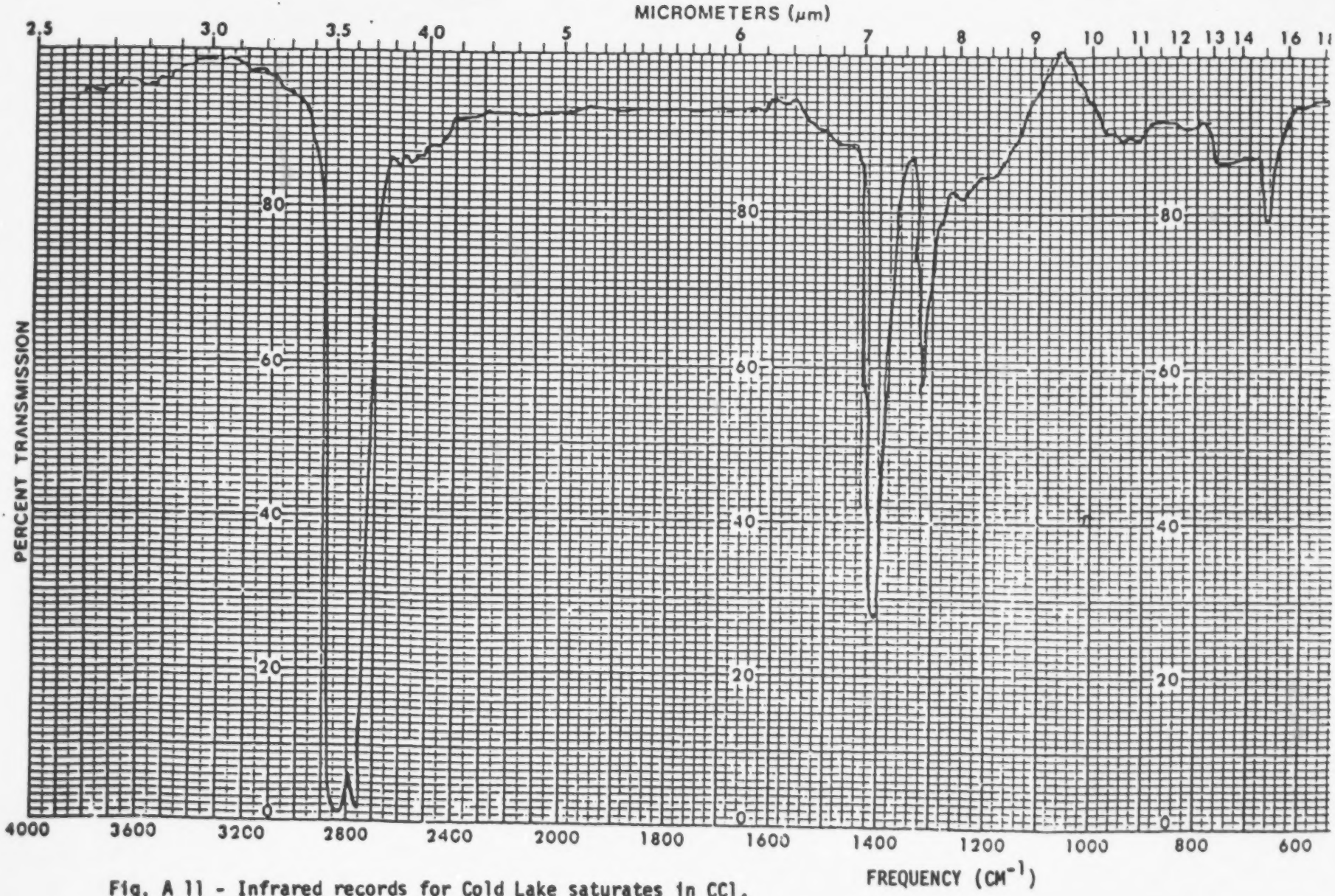


Fig. A 11 - Infrared records for Cold Lake saturates in CCl_4

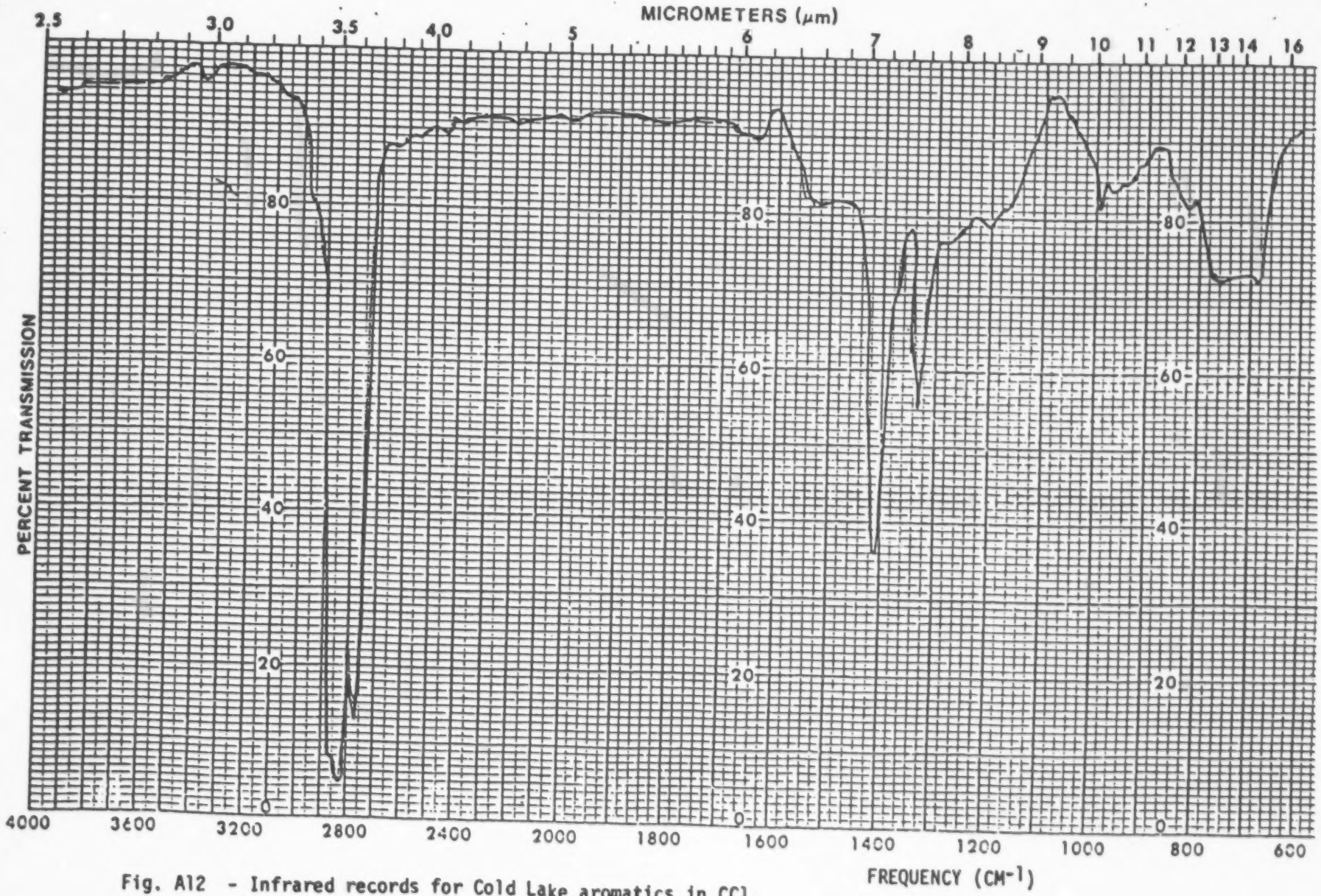


Fig. A12 - Infrared records for Cold Lake aromatics in CCl_4

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4. Isolation of representative saturates fraction from high-olefinic petroleum naphths - ASTM D.2003/81.
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